



DECLARATION

I, KATSUHIKO KIMURA, a Japanese Patent Attorney registered No. 13439, of Okabe International Patent Office at No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo, Japan, hereby declare that I have a thorough knowledge of Japanese and English languages, and that the attached pages contain a correct translation into English of the priority documents of Japanese Patent Application No. 2000-240492 filed on August 8, 2000 in the name of CANON KABUSHIKI KAISHA.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 29th day of August, 2006

A handwritten signature in black ink, appearing to read "H. Kimura", written over a horizontal line.

KATSUHIKO KIMURA

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy
of the following application as filed with this office.

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Application Number: Japanese Patent Application
No. 2000-240492

Applicant(s): CANON KABUSHIKI KAISHA

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Commissioner,
Patent Office

KOZO OIKAWA

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2000-240492

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[Title of the Invention]	INK, INK-JET RECORDING PROCESS, RECORDED ARTICLE, RECORDING UNIT, INK CARTRIDGE AND INK-JET RECORDING APPARATUS
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[Material]	Drawings	1
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[Name of the Document]	Specification
[Title of the Invention]	Ink, Ink-Jet Recording Process, Recorded Article, Recording Unit, Ink Cartridge and Ink-Jet Recording Apparatus

[What is Claimed is]

[Claim 1]

An ink at least comprising: two combined organic compounds which are incompatible with each other; a coloring material exhibiting fluorescence properties of not more than 1.5 % by weight; glycol having a vapor pressure not higher than that of diethylene glycol; and a liquid medium for dissolving or dispersing the above materials therein.

[Claim 2]

The ink according to Claim 1, wherein the ink is a water-based ink.

[Claim 3]

The ink according to Claim 1, wherein the coloring material exhibiting fluorescence properties is a coloring material to be dissolved or dispersed in water.

[Claim 4]

The ink according to Claim 3, wherein the coloring material exhibiting fluorescence properties is a dye having water solubility.

[Claim 5]

The ink according to Claim 1, which is applied to an ink jet recording.

[Claim 6]

The ink according to Claim 1, wherein the content of the coloring material exhibiting fluorescence properties in the ink is at least a concentration sufficient for the coloring material to exhibit the maximum fluorescence intensity in the ink.

[Claim 7]

The ink according to Claim 6, wherein the content of the coloring material exhibiting fluorescence properties in the ink is at least a concentration sufficient for the coloring material to exhibit the maximum fluorescence intensity in a state in which the coloring material is dissolved or dispersed in water.

[Claim 8]

The ink according to Claim 1, wherein the content of the coloring material exhibiting fluorescence properties in the ink is not more than 1.0% by weight.

[Claim 9]

The ink according to Claim 1, which is obtained by combining two organic compounds incompatible with each other, wherein one of the organic compounds has a solubility parameter value of not less than 15, and the other has a solubility parameter value of not more than 13.

[Claim 10]

The ink according to Claim 1, wherein the two

organic compounds which are incompatible with each other are nonpolar compounds.

[Claim 11]

The ink according to Claim 1, wherein the two organic compounds which are incompatible with each other are both water-soluble.

[Claim 12]

The ink according to Claim 11, wherein the two organic compounds which are incompatible with each other are both liquid.

[Claim 13]

The ink according to Claim 1, wherein the two organic compounds which are incompatible with each other have a glycerol group.

[Claim 14]

The ink according to Claim 13, wherein the organic compound having a glycerol group has 3 hydroxyl groups or more.

[Claim 15]

The ink according to Claim 13, which is liquid at normal temperature.

[Claim 16]

The ink according to Claim 1, wherein one of the two organic compounds which are incompatible with each other is a nonionic surfactant.

[Claim 17]

The ink according to Claim 16, wherein the nonionic

surfactant is liquid at normal temperature.

[Claim 18]

The ink according to Claim 16, wherein HLB of the nonionic surfactant is not more than 13.

[Claim 19]

The ink according to Claim 18, wherein the nonionic surfactant is contained in the ink in such an amount that the nonionic surfactant is not separated at an interface of an aqueous solution in a state of the aqueous solution.

[Claim 20]

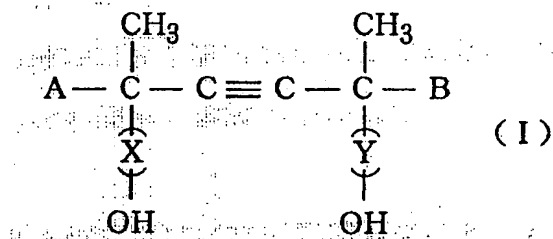
The ink according to Claim 19, wherein the nonionic surfactant is contained in the ink in such an amount that the nonionic surfactant is not separated at an interface of the ink in a state of an ink from which the coloring material has been removed.

[Claim 21]

The ink according to Claim 16, wherein the nonionic surfactant has an acetylene group.

[Claim 22]

The ink according to Claim 21, wherein the nonionic surfactant has a structure represented by the following general formula (I)



wherein A and B are, independently of each other, C_nH_{2n+1} (n being an integer of 1 to 10), and X and Y are, independently of each other, a ring-opening ethylene oxide unit and/or a ring-opening propylene oxide unit.

[Claim 23]

The ink according to Claim 16, wherein the nonionic surfactant is contained in a proportion of not less than 1 % by weight in the ink.

[Claim 24]

The ink according to Claim 1, which further comprises a monohydric alcohol.

[Claim 25]

The ink according to Claim 1, which further comprises a coloring material exhibiting no fluorescence properties.

[Claim 26]

The ink according to Claim 25, wherein the coloring material exhibiting no fluorescence properties is a coloring material having water solubility.

[Claim 27]

The ink according to Claim 25, wherein the coloring material exhibiting no fluorescence properties is a coloring material directly coloring a recording medium.

[Claim 28]

The ink according to Claim 25, wherein the coloring material exhibiting no fluorescence properties is an azo dye.

[Claim 29]

The ink according to Claim 25, wherein the content of the coloring material exhibiting no fluorescence properties in the ink is not lower than the content of the coloring material exhibiting fluorescence in the ink.

[Claim 30]

The ink according to Claim 25, wherein the coloring material exhibiting no fluorescence properties has a carboxyl group or its salt group.

[Claim 31]

The ink according to Claim 25, wherein the counter ion to the hydrophilic group of the coloring material exhibiting no fluorescence properties is ammonium.

[Claim 32]

The ink according to Claim 1, which further comprises at least one selected from urea and urea derivatives.

[Claim 33]

The ink according to Claim 32, wherein the urea derivative is not a cyclic compound.

[Claim 34]

The ink according to Claim 32, wherein the urea derivative is at least one selected from the group consisting of alkyl derivatives of urea and ethylene oxide and/or propylene oxide adducts of urea.

[Claim 35]

The ink according to Claim 1, wherein the ink from

which the coloring material and additives have been removed is nonionic.

[Claim 36]

The ink according to Claim 1, wherein the surface tension of the ink is not more than 40 dyn/cm.

[Claim 37]

The ink according to Claim 1, wherein the ink has the pH of not less than 8.

[Claim 38]

The ink according to Claim 1, wherein the coloring material of the ink has two counter ions, one of which is an ammonium ion and the other is an alkali metal ion.

[Claim 39]

The ink according to Claim 1, which has a maximum wavelength for excitation and a fluorescence maximum wavelength, and the maximum wavelength for excitation is shorter than the fluorescence maximum wavelength.

[Claim 40]

An ink-jet recording process for obtaining a recorded article by ejecting ink droplets from an orifice in response to recording signals and effecting recording on a recording medium, wherein the step comprises a sub-step of using the ink according to any one of Claims 1 to 39.

[Claim 41]

The ink-jet recording process according to Claim 40, wherein the step comprises a sub-step of applying thermal energy to the ink to eject the ink from an orifice,

so as to eject ink droplets.

[Claim 42]

A recorded article which is obtained by the ink-jet recording process according to Claim 40, wherein the fluorescence intensity of the recorded article formed on a wood-free paper has a proportional relationship to the water content in the wood-free paper.

[Claim 43]

The recorded article according to Claim 42, which has a maximum wavelength for excitation and a fluorescence maximum wavelength, and the maximum wavelength for excitation is shorter than the fluorescence maximum wavelength.

[Claim 44]

A recording unit comprising an ink container containing ink and a head portion for ejecting the ink as ink droplets, wherein said ink is at least one selected from the inks according to any one of Claims 1 to 39.

[Claim 45]

The recording unit according to Claim 44, wherein the head portion has a construction in which thermal energy is applied to the ink to eject the ink droplets.

[Claim 46]

The recording unit according to Claim 44, wherein the ink container comprises a polyolefin.

[Claim 47]

The recording unit according to Claim 46, wherein

the ink container has an ink holding member therein.

[Claim 48]

The recording unit according to Claim 47, wherein the ink holding member comprises at least one selected from the group consisting of polyurethane, cellulose, polyvinyl acetate and polyolefin.

[Claim 49]

The recording unit according to Claim 47, wherein the ink holding member comprises a polymer of inorganic compound(s).

[Claim 50]

The recording unit according to Claim 48, wherein the ink holding member comprises a porous material.

[Claim 51]

The recording unit according to Claim 50, wherein the ink holding member has a surface being in contact with the ink container.

[Claim 52]

The recording unit according to Claim 45, wherein the ink holding member has a multi-layer structure.

[Claim 53]

The recording unit according to Claim 50, wherein the direction of the multi-layer arrangement of the multi-layer structure is aligned in an ink discharging direction of the ink container.

[Claim 54]

The recording unit according to Claim 53, wherein

the ink holding member has a contact surface with the ink container.

[Claim 55]

The recording unit according to Claim 47, wherein the ink holding member is composed of fiber flocculate.

[Claim 56]

The recording unit according to Claim 55, wherein the fiber flocculate is aligned in an ink discharging direction of the ink container.

[Claim 57]

The recording unit according to Claim 56, wherein the ink holding member has a contact surface with the ink container.

[Claim 58]

An ink cartridge comprising an ink container containing ink, wherein said ink is at least one selected from the inks according to any one of Claims 1 to 39.

[Claim 59]

The ink cartridge according to Claim 58, wherein the ink container comprises a polyolefin.

[Claim 60]

The ink cartridge according to Claim 59, wherein the ink container has an ink holding member therein.

[Claim 61]

The ink cartridge according to Claim 60, wherein the ink holding member comprises at least one selected from the group consisting of polyurethane, cellulose, polyvinyl

acetate and polyolefin.

[Claim 62]

The ink cartridge according to Claim 61, wherein the ink holding member is composed of a polymer of inorganic compound(s).

[Claim 63]

The ink cartridge according to Claim 60, wherein the ink holding member has a multi-layer structure.

[Claim 64]

The ink cartridge according to Claim 63, wherein the ink holding member has a contact surface with the ink container.

[Claim 65]

The ink cartridge according to Claim 60, wherein the ink holding member has a multi-layer structure.

[Claim 66]

The ink cartridge according to Claim 65, wherein the direction of the multi-layer arrangement of the multi-layer structure is aligned in an ink discharging direction of the ink container.

[Claim 67]

The ink cartridge according to Claim 66, wherein the ink holding member has a contact surface with the ink container.

[Claim 68]

The ink cartridge according to Claim 60, wherein the ink holding member is composed of fiber flocculate.

[Claim 69]

The ink cartridge according to Claim 68, wherein the fiber flocculate is aligned in an ink discharging direction of the ink container.

[Claim 70]

The ink cartridge according to Claim 69, wherein the ink holding member has a contact surface with the ink container.

[Claim 71]

An ink-jet recording apparatus comprising an ink container containing ink and a head portion for ejecting the ink as ink droplets, wherein said ink is at least one selected from the inks according to any one of Claims 1 to 39.

[Claim 72]

The ink-jet recording apparatus according to Claim 71, wherein the recording unit is at least one selected from the recording units according to any one of Claims 45 to 57.

[Claim 73]

An ink-jet recording apparatus comprising a recording unit for ejecting ink droplets, an ink cartridge having an ink container containing the ink and an ink supply portion for supplying the ink from the ink cartridge to a recording head, wherein said ink is at least one selected from the inks according to any one of Claims 1 to 39.

[Claim 74]

The ink-jet recording apparatus according to Claim 73, wherein the recording unit is at least one selected from the recording units according to any one of Claims 44 to 57.

[Claim 75]

The ink-jet recording apparatus according to Claim 71, wherein the ink cartridge is at least one selected from the ink cartridges according to any one of Claims 58 to 70.

[Detailed Description of the Invention]

[0001]

[Field of the Industrial Utilization]

The present invention relates to an ink, an ink-jet recording process using such an ink, a recorded article obtained by such a recording process and instruments using such an ink, and particularly to an ink which can enhance fluorescence intensity and provide a recorded article good in record quality including stability, reliability and coloring ability to look at, an ink-jet recording process using such an ink, and instruments using such an ink.

[0002]

[Prior Art]

Various investigations and reports have heretofore been made on inks for writing utensils and inks for ink-jet. In particular, in order to enhance the quality of recorded articles, including fluorescence intensity and coloring ability, such various proposals as described above have been made. For example, proposals of coloring materials and the

like each having a novel structure, which are suitable for use in inks for the above-described use applications, proposals of inks using a coloring material (hereinafter referred to as "fluorescent coloring material") exhibiting fluorescence properties as a main coloring material, and proposals as to the combined use of a fluorescent coloring material as a coloring material for inks have been made. In particular, the proposals as to inks, which pay attention to the fluorescence properties of fluorescent coloring materials, include Japanese Patent Application Laid-Open Nos. 8-151545, 9-132729, 10-193775, 10-298462 and 10-298467, and Japanese Patent No. 0,233,038, and novel recording processes and fluorescent coloring materials have been proposed therein.

[0003]

In addition, the proposals as to the use of fluorescent coloring materials include Japanese Patent Application Laid-Open Nos. 5-293976, 6-191143, 6-322307, 7-009755, 7-305013, 8-053639, 9-003375, 9-01294, 9-137097, 9-137098, 9-137099, 9-165539, 9-241565, 9-255904, 9-286939, 10-007962, 10-183043, 11-080639, 11-320921 and 2000-038529, and Japanese Patent No. 2995853.

[0004]

In recent years, the use applications of fluorescent coloring materials have not been limited to the mere formation of beautiful color images heretofore conducted, and there have been proposed, for example,

technical development that fluorescence properties are imparted to an ink, information such as characters, numerals, marks and/or bar codes is recorded on a recording medium with such an ink, and the fluorescent ink is caused to emit light by irradiating the recording medium with ultraviolet light having a proper wavelength, thereby imparting another information (for example, security information) than visible information. Accordingly, there is room to widen the use applications of inks exhibiting fluorescence properties in many fields, and there is a strong demand for development of inks which are stable, reliable, high in fluorescence intensity and excelling in coloring ability.

[0005]

[Problems to be Solved by the Invention]

With respect to the coloring ability of an ink on a recording medium, however, only chromaticity (L^*, a^*, b^*) that is used as a measure of colors has heretofore been considered. Even when a fluorescent color material is used, design is also made according to the conventional measure under the circumstances. Therefore, it has been hard to say that the fluorescence properties of the coloring material are fully utilized. More specifically, even in the above-described various proposals making use of the fluorescent coloring materials, in the standpoint of the coloring ability of the coloring materials, the fluorescent coloring materials are used on the basis of only the viewpoint of (L^*, a^*, b^*), not the viewpoint of the

fluorescence properties, or attention is paid to the fluorescence properties of the coloring materials, but no attention is paid to the color developing properties of fluorescence, in other words, the interfacial properties of the fluorescence. Therefore, such proposals have not fully made the best use of the fluorescence properties of the coloring materials.

[0006]

It is accordingly an object of the present invention to provide an ink which can provide a recorded article obtainable by fully making good use of the fluorescence properties of the coloring material, and being excellent in print quality including coloring ability, said ink being capable of enhancing the stability and reliability of the recorded article, an ink-jet recording process using such an ink, a recorded article obtained by the recording process, and instruments using such an ink.

[0007]

[Means for Solving the Problems]

The above object is achieved by the present invention as described below. That is, the present invention provides an ink at least comprising: two combined organic compounds which are incompatible with each other; a coloring material exhibiting fluorescence properties of not more than 1.5 % by weight; glycol having a vapor pressure not higher than that of diethylene glycol; and a liquid medium for dissolving or dispersing the above organic

components and the coloring material therein, as well as an ink-jet recording process employing such ink, a recorded article obtained by such a process, and equipment utilizing such ink.

[0008]

[Description of the Preferred Embodiments]

The present invention will hereinafter be described in more detail by the preferred embodiments of the invention.

The mechanism that a recorded article good in stability and reliability and moreover good in coloring ability by fully making good use of the fluorescence properties of the ink with less deterioration of the fluorescence intensity with time can be provided by the ink according to this invention will be first described.

The present inventors have considered a wide variety of mechanisms for developing inks which can provide recorded articles good in stability, reliability and coloring ability and carried out an investigation and identification as to a wide variety of coloring materials and ink compositions. As a result, the inventors have been led to a new fact that when 2 compounds which are incompatible with each other are used as components for an ink, the coloring ability of the resulting recorded article can be made good, thus leading to completion of the present invention. More specifically, it has been found that when an ink at least comprising 2 organic compounds which are

incompatible with each other, a coloring material exhibiting fluorescence, and a liquid medium dissolving or dispersing the two organic compounds, and the coloring material exhibiting fluorescence therein is used, the quality of the resulting recorded article, including fluorescence intensity and coloring ability is improved when the ink is applied on to a recording medium, a recorded article good in stability and reliability is provided, and particularly, such an ink exhibits good results when it is used for ink-jet recording. In addition, it has been found that from the viewpoint of the fluorescence intensity of the recorded article, the ink according to the present invention having the above-described constitution can markedly enhance the fluorescence intensity compared with a recorded article formed with the conventional fluorescent ink.

[0009]

When a mechanism for an ink which can provide a recorded article good in stability and reliability and moreover good in fluorescence intensity, coloring ability, etc. is considered, attention is generally paid to how to dissolve or disperse a coloring material uniformly and in a good state in the ink as a means for enhancing the fluorescence and coloring ability of the recorded article. In other words, an investigation is made as to how to do away with aggregation of coloring material molecules or dispersed particles in the ink to make the coloring material

molecules or dispersed particles small, for example, whether the absorbance of the ink can be enhanced and whether the absorbance can be retained in a high state when consideration is made on the ink, and the ink is designed. It is attempted to make the coloring material molecules or dispersed particles in the ink applied on to a recording medium hard to aggregate by making the design of the ink in such a manner, thereby making the coloring ability and fluorescence properties of the coloring material good.

[0010]

On the other hand, with respect to recorded articles (prints) formed by applying an ink on to recording media, the present inventors have carried out again an investigation as to the state of the ink on the recording media, and a wide variety of recorded articles in the world, consideration has been conducted repeatedly. As a result, the inventors have first paid attention to the facts that there is an interface between a recording medium and an ink on the recording medium in any recorded article though it may not be sharp, and that the ink on the recording medium is present in a state that the ink has possessed an interface with the atmosphere. Further, attention has been paid to the facts that when recording is conducted on, for example, wood-free paper, the coloring ability of a coloring material to look at tends to be deteriorated when the penetration of the ink is enhanced, and that when recording is conducted on a back coated film, or a recorded article is laminated

thereon, the coloring ability of the coloring material to look at is improved. From the facts described above, an investigation has been made from the viewpoints of how to form the interfacial state of the ink to the atmosphere, in which the coloring ability of the coloring material becomes good on the recording medium, after recording, and how to retain such a state, thus leading to completion of the present invention..

[0011]

The present inventors consider that the ink according to this invention can markedly enhance the fluorescence properties and coloring ability of the resulting recorded article by the following specific mechanism.

In the ink according to this embodiment, as illustrated in Fig. 7, the individual components are present in a uniform state that they have been fully dissolved or dispersed in the liquid medium in the state of the ink. When such an ink droplet is applied on the recording medium to conduct recording as illustrated in Fig. 8, a part (particularly, liquid medium) of the ink components evaporates into the atmosphere or penetrates into the recording medium to diffuse, as illustrated in Fig. 9, whereby the constitution and compositional ratio of the ink on the recording medium are changed. As a result, the two organic compounds incompatible with each other, which have been stably present in the state of the ink, undergo phase

separation in a lamellar state on the recording medium to form an interface by the ink components between the ink and the atmosphere as illustrated in Fig. 10. Therefore, a state as if a recorded article has been laminated is created. Fig. 11 typically expresses the state shown in Fig. 10 for simplifying it. As a result, in the recorded article formed by the ink according to the present invention, the layer having a stable thickness is formed by the development of the liquid-liquid interface. Therefore, the reflection of light can be effectively developed, and so coloring ability including fluorescence intensity is made good, thereby becoming an effective means for markedly enhancing the fluorescence properties and coloring ability of the recorded article.

[0012]

According to a further investigation by the present inventors, it has been found that water is preferably used as the liquid medium in order that the two organic compounds incompatible with each other are caused to coexist in a substantially uniform state in the ink. More specifically, when water is used as the liquid medium, a wider variety of compounds may be used compared with other liquid media, so that not only room for selection of constituent materials of the ink can be widened, but also the quality of the resulting recorded article formed with wood-free paper is hard to be deteriorated compared with inks making use of a non-aqueous liquid medium, and the liquid medium can also

be removed by penetration into the wood-free paper, and moreover the liquid medium is stable to evaporation. The use of water is hence preferred even from this point of view.
[0013]

Furthermore, the ink according to the present invention comprises glycol having a vapor pressure not higher than that of diethylene glycol. With the ink of the present invention employing such glycol, it is possible to obtain another excellent effects that the coloring ability including the fluorescence intensity becomes more excellent, that the fluorescence properties or the coloring ability of a recorded article are conspicuously enhanced, and that the defect of the recorded article exhibiting the fluorescence properties that the fluorescence intensity of the fluorescent coloring material is deteriorated with time can be effectively suppressed. The present inventors consider that these effects are brought about the evaporation which occurs on the recorded material of the glycol having the vapor pressure equal to or lower than that of the diethylene glycol. More specifically, the evaporation speed of the glycol having the vapor pressure equal to or lower than that diethylene glycol is slower than that of water, which however results in that, in case of the ink of the present invention comprising the above-described compounds, the evaporation of the glycol having the vapor pressure equal to or lower than that of diethylene glycol is suppressed even when water or the like evaporates

after the ink is recorded on the recording medium. Consequently, since a layer which is formed when the two organic compounds incompatible with each other undergo phase separation is formed with time, it is possible to effectively suppress the deterioration with time of the fluorescence intensity of the fluorescent coloring material with light applied thereon. In case the ink of the present invention comprising the glycol having the vapor pressure equal to or lower than that of diethylene glycol is used, it is possible to conspicuously suppress the deterioration of the fluorescence intensity of the recorded article with time, compared with a conventional recorded article.

[0014]

The components and the like of the ink according to this invention that the excellent effects are achieved by the mechanism described above will hereinafter be described.

The two organic compounds incompatible with each other, which constitute the ink according to this invention, mean those undergoing phase separation in a lamellar state like, for example, water and oil when only the organic compounds are mixed.

The liquid medium for these organic compounds are selected from among a wide variety of liquids in view of the combination of the two organic compound in compatible with each other and its compatibility with these organic compounds. However, it is particularly preferred that the

liquid medium be determined to be water. The reasons for it include stability of the resulting ink, and besides problems of quality and the like when a non-aqueous liquid medium is used, which have been mentioned in the above-described mechanism, and ease of selecting the two organic compound compatible with each other.

[0015]

The two organic compound in compatible with each other may be any compounds so far as they undergo phase separation in a lamellar state like, for example, water and oil when only the organic compounds are mixed, as described above. However, for example, those one of which has a solubility parameter of at least 15 and the other of which has a solubility parameter of at most 13 are preferred. If the solubility parameter values of both compounds are too close, they become liable to be compatible with each other, and so the effects of the present invention may be hard to develop in some cases. Incidentally, the solubility parameter values as shown herein are values determined in accordance with the Fedors method.

[0016]

One of the two organic compound incompatible with each other preferably has a glycerol group. The glycerol group has strong hydrating force and is easy to serve as the compound on the water side of "water and oil" shown in the above-described specific example of the phenomenon of the present invention. Among such compounds, sugar

alcohols as monomers, such as glycerol, xylitol and erythritol, and sugar alcohols as dimers and trimers, such as glycerol and diglycerol.

[0017]

Further, ethylene oxide, propylene oxide or combination thereof may be added as substituents to the compounds mentioned above. Among these, those having at least 3 hydroxyl groups and those liquid at normal temperature are particularly preferred. The content of these compounds in the ink is preferably controlled to 1.0 to 30 % by weight, particularly 5.0 to 20 % by weight based on the total weight of the ink. However, the present invention is not limited thereto according to a recording medium used.

[0018]

The other of the two organic compounds incompatible with each other for constituting the ink of the present invention will now be described. As a compound corresponding to the oil which undergoes phase separation in a lamellar state when it is mixed with the former compound against the former compound described above, a nonionic compound is preferably used. On the other hand, when a nonionic solution or a surfactant having a polar group is used, though such solution or surfactant undergoes phase separation in a lamellar state, it becomes difficult to develop the above-described mechanism. Particularly, an adverse influence may be generated when other components are mixed in the ink.

[0019]

Among the nonionic surfactants, those having an HLB of at most 13 may preferably be used. In general, those having an HLB exceeding 13 become too hydrophilic. However, the 2 organic compounds incompatible with each other, which are components of the ink according to this invention, undergo phase separation on the surface of a recording medium to form an interface by the ink components between the ink and the atmosphere, thereby making it difficult to develop the above-described mechanism of making the coloring ability including fluorescence intensity good.

[0020]

The nonionic surfactant which is used as the constituent component of the ink of the present invention preferably undergoes no phase separation in a state of an aqueous solution from the aqueous solution. If a surfactant undergoing phase separation from the aqueous solution, when, for example, an ink is prepared with water as a preferable liquid medium, the ink becomes unstable unpreferably. This apparently indicates that the nonionic surfactant is preferably used in a state uniformly dissolved or dispersed in water. In particular, a nonionic surfactant, which forms a state of an emulsion in water, may preferably be selected. It is further preferred that the content of the nonionic surfactant in the ink be selected within a range sufficient to retain the emulsion state in the state of the aqueous solution, since the fear of stability in the ink is eliminated.

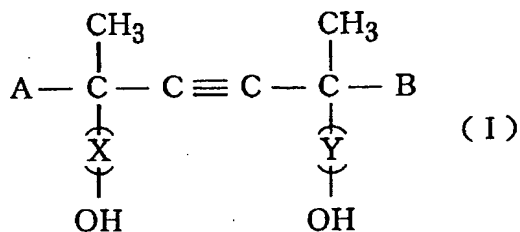
[0021]

The specific content of the nonionic surfactant in the ink according to this invention is preferably controlled to at least 1 % by weight, more preferably 1 to 20 % by weight based on the total weight of the ink. When the content is not more than 1 % by weight, the above-described mechanism can be less developed. When the content is 20% by weight or more, the balance of print quality, for example, balance between feathering, which is whisker-like blur, and fixing ability or concentration can be prevented from being deteriorated.

[0022]

Among the nonionic surfactants satisfying the above-described requirements, particularly preferable compounds as a constituent component of the ink of the present invention include compounds represented by the following general formula (I) and the following compounds (II) to (VII).

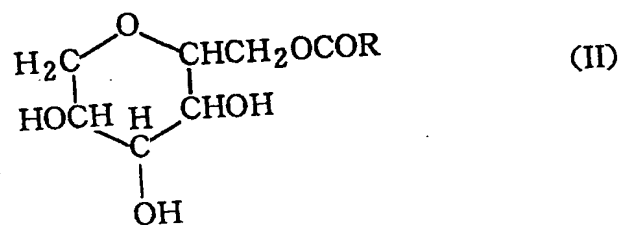
[0023]



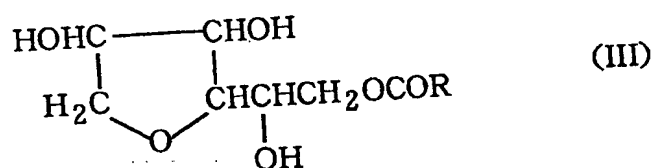
wherein A and B are, independently of each other, $\text{C}_n\text{H}_{2n+1}$ (n being an integer of 1 to 10), and X and Y are, independently of each other, a ring-opening ethylene oxide unit and/or

a ring-opening propylene oxide unit.

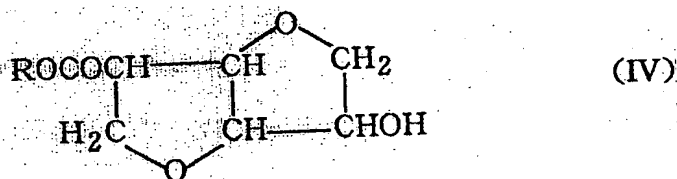
[0024]



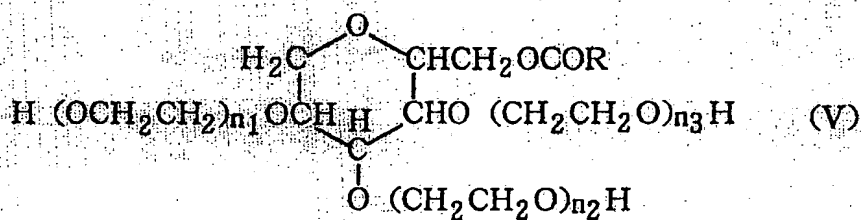
1,5-Sorbitan ester



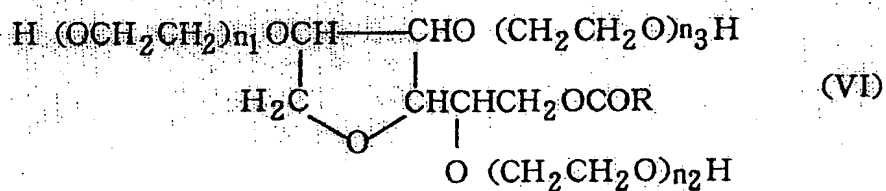
1,4-Sorbitan ester



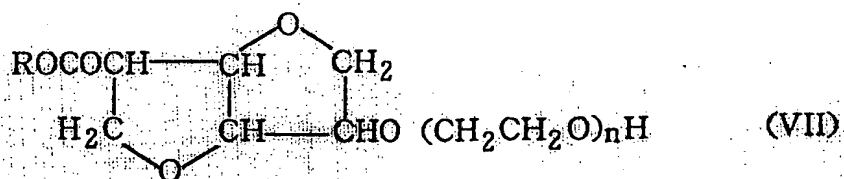
Sorbite ester



wherein n_1 , n_2 and n_3 are integers.



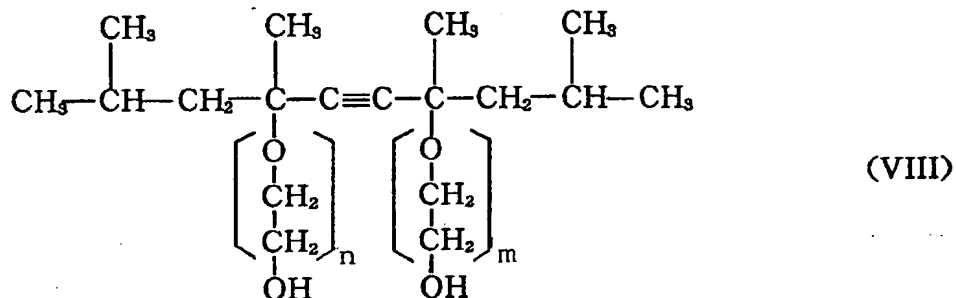
wherein n_1 , n_2 and n_3 are integers.



(R: alkyl group of a fatty acid)

[0025]

Among the nonionic surfactants represented by the general formula (I), compounds represented by the following general formula (VIII) are particularly preferred.



wherein m and n are integers.

[0026]

Though the two organic compounds incompatible with each other described above are used for constituting the ink of the present invention, a fluorescent coloring material is additionally used in a content of 1.5% by weight or less in the ink. The effect by the above-described mechanism is fully developed when the fluorescent coloring material is used. Further, since the ink according to this invention tends to exhibit better results in an aqueous system making use of water as the liquid medium by virtue of the above-described reasons, it is preferred that coloring materials soluble or dispersed in water be used as the fluorescent coloring material used in the ink according to this invention. Further, as the fluorescent coloring material, it is preferable to use a water-soluble

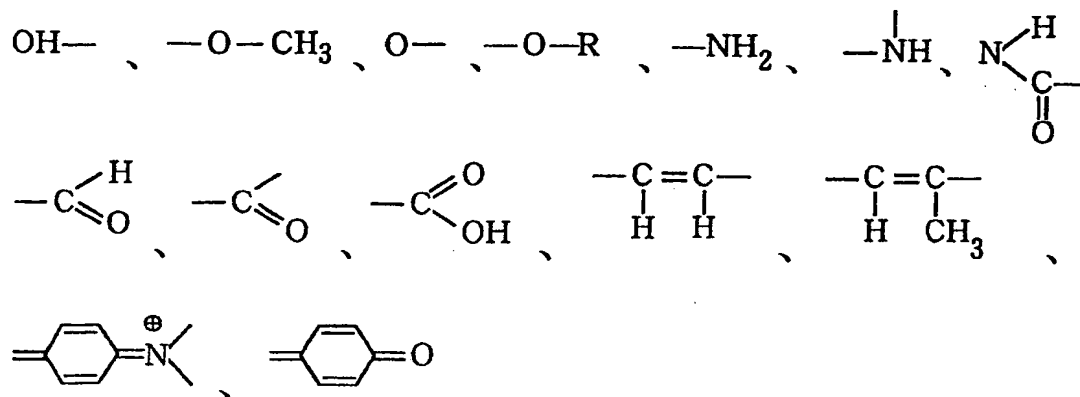
dye.

[0027]

In this case, the coloring materials soluble or dispersed in water include, for example, coloring materials (for example, dyes) soluble in water by themselves, and also coloring materials which are dissolved in water by a method of emulsifying them in water by treating the surfaces thereof, or the like. However, a technique that a coloring material is dispersed by using a resin as a dispersing agent, like pigment dispersion is not included. The reason for it is that this type of coloring material is hard to develop the effect by the above-described mechanism, and moreover it may not be said to be a very preferable selection from the viewpoint of reliability of the resulting ink.

[0028]

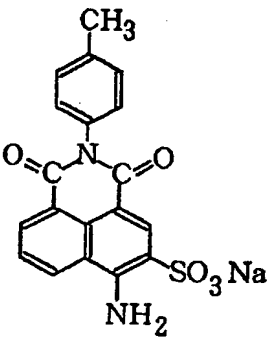
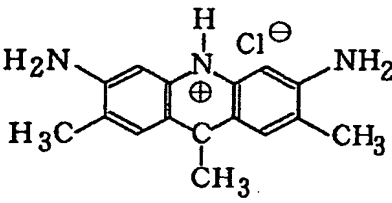
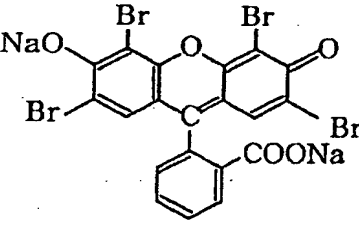
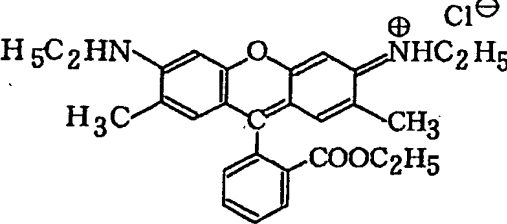
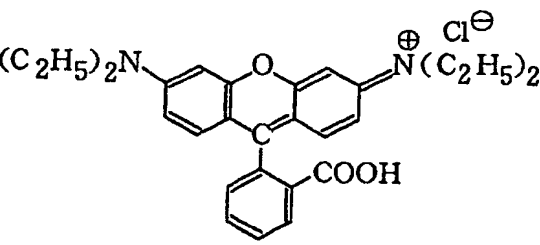
As the fluorescent coloring materials used for constituting the ink according to the present invention are particularly preferred those containing any of the following atomic groups



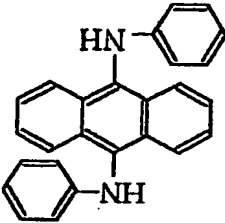
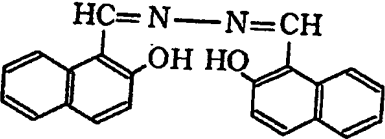
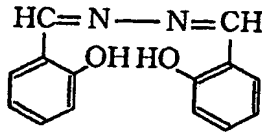
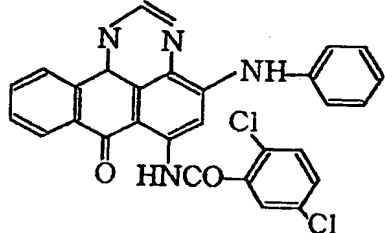
[0029]

Specific examples of the fluorescent coloring

materials containing any of such atomic groups as described above include the following compounds.

Name of dye	Structure	Color under daylight	Fluorescent color
Brilliant-sulfoflavin FF (C.I. 56205)		Yellow	Green to yellowish green
Basic Yellow HG (C.I. 46040)		Yellow	Greenish yellow to yellow
Eosine (C.I. 45380)		Red	Yellow to orange
Rhodamine 6G (C.I. 45160)		Red	Yellow to orange
Rhodamine B (C.I. 45170)		Pink	Orange to red

[0030]

Name of pigment	Structure
Lumogen L Yellow	
Lumogen L Brilliant Yellow	
Lumogen L Yellow Orange	
Lumogen L Red Orange	

[0031]

The content of such fluorescent coloring materials as mentioned above in the ink is preferably controlled to at most 1.5 % by weight. The fluorescent coloring material has a nature that when its content in the ink exceeds a certain value, the fluorescence intensity of the ink is

lowered (the phenomenon refers to as concentration quenching). For this reason, the concentration quenching cannot be prevented by the above-described mechanism if the concentration exceeds 1.5 % by weight.

[0032]

Furthermore, the ink according to the present invention comprises as its constituent component the glycol having the vapor pressure equal to or lower than that of diethylene glycol. As described above, since such a compound is employed in the ink, it becomes possible to effectively suppress the defect of a recorded article exhibiting the fluorescence properties including the fluorescence intensity of the conventional fluorescent coloring material with light applied thereon which is deteriorated with time. As compounds having the vapor pressure of not higher than that of diethylene glycol serving as a constituent component of the ink of the present invention include ethylene glycol, diethylene glycol, triethylene glycol, tripropylene glycol, etc.

[0033]

From the viewpoint of the stability of the ink, it is preferable that a monohydric alcohol should be also additionally used in combination in the ink according to this invention. The monohydric alcohol has an effect to mix water with oil like, for example, dehydration of gasoline. This indicates that the monohydric alcohol is preferably used in combination in the ink from the viewpoint of the stability of the ink upon development of the above-described

mechanism. In addition, the monohydric alcohol has a good effect for evaporation and penetration into a recording medium when the resulting ink is applied to the recording medium. Therefore, the monohydric alcohol is useful for better developing the effect of the present invention. The content of the monohydric alcohol in the ink according to this invention is 0.1 to 20 % by weight, preferably 0.5 to 10 % by weight based on the total weight of the ink.

Specific examples of the monohydric alcohol usable as a component of the inks according to this invention include ethanol, isopropanol and n-butanol.

[0034]

A water-holding agent may also be used in combination in the inks according to this invention. As the water-holding agent, a compound selected from urea and urea derivatives may be preferably used. When a compound selected from urea and urea derivatives is contained in the ink, the stability of the ink is improved. More specifically, when the compound selected from urea and urea derivatives is contained, the mechanism that the two organic compounds incompatible with each other in the ink undergo phase separation in a lamellar state is prevented from being developed at a gas-liquid interface in a state of an ink. In addition, the selected from urea and urea derivatives also has an effect as a solvent aid, and so the use of such a compound is also preferred from the viewpoint of stability of the ink.

When the recording medium is, for example,

wood-free paper, the effect by the mechanism according to the present invention is easy to develop due to the water-holding ability of the wood-free paper. More specifically, it is expected that water is held in the recording medium, whereby the time when the ink components are released into the recording medium and the atmosphere can be slowed, and so the phase separation of the two organic compounds incompatible with each other in the lamellar state is made with good results.

[0035]

As the urea derivatives, compounds other than cyclic compounds are preferred, and at least one selected from alkyl derivatives of urea and ethylene oxide and/or propylene oxide adducts of urea, or a compound suitably selected from derived compounds modified by at least two of the above derivative groups is preferably used. However, the selection varies according to the amounts and kinds of individual components making up the ink. That soluble in water is preferably used. No particular limitation is imposed on the amount of such a compound used. However, it is generally contained in a range of preferably from 0.1 to 15 % by weight, more preferably from 0.1 to 10 % by weight based on the total weight of the ink.

[0036]

In the inks according to this invention, may be contained various additives such as a water-soluble organic solvent, a surfactant, a rust preventive, a preservative, a mildewproofing agent, an antioxidant, anti-reducing agent,

an evaporation accelerator, a chelating agent, a water-soluble polymer and a pH adjustor, as needed.

[0037]

As the liquid medium used in the inks according to this invention, water is preferably used as described above. More preferred is a mixture of water and a water-soluble organic solvent. Specific examples of the water-soluble organic solvent include amides such as dimethylformamide and dimethylacetamide; ketones such as acetone; ethers such as tetrahydrofuran and dioxane; polyalkylene glycols such as polyethylene glycol and polypropylene glycol; alkylene glycols the alkylene moiety of which has 2 to 6 carbon atoms, such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, thiodiglycol, hexylene glycol and diethylene glycol; 1,2,6-hexanetriol; glycerol; lower alkyl ethers of polyhydric alcohols, such as ethylene glycol monomethyl (or monoethyl) ether, diethylene glycol monomethyl (or monoethyl) ether and triethylene glycol monomethyl (or monoethyl) ether; N-methyl-2-pyrrolidone; 1,3-dimethyl-2-imidazolidinone; triethanolamine; sulfolane; dimethyl sulfoxide; cyclic amide compounds such as 2-pyrrolidone and ϵ -caprolactam; and imide compounds such as succinimide.

[0038]

In the ink according to the present invention, it is particularly preferable to employ a glycol having a vapor pressure lower than that of diethylene glycol in combination. As, when the ink droplets are fixed on the recording medium,

usually the ink components permeate or are dispersed in a wood-free paper, in which case the effects of the present invention are exhibited. On this occasion, it is estimated that, if a liquid glycol having the vapor pressure lower than that of diethylene glycol is employed in combination, the exhibition of the effects of the present invention is delayed under an influence of this glycol, so that a stable layer is formed to emit this glycol further to the atmospheric side, thereby obtaining the effects of the present invention with excellency.

[0039]

The content of such a water-soluble organic solvent as described above is generally within a range of preferably from 1 to 40 % by weight, more preferably from 3 to 30 % by weight based on the total weight of the ink. The content of water in the ink is generally within a range of from 30 to 95 % by weight based on the total weight of the ink. If the content is lower than 30 % by weight, the solubility of the coloring material and the like becomes deteriorated, and the viscosity of the resulting ink is also increased. It is hence not preferable to use water in such a low proportion. If the content of water exceeds 95 % by weight on the other hand, an evaporating component is too great to satisfy sufficient crusting property.

[0040]

In the inks according to this invention, a coloring material exhibiting no fluorescence properties may be contained to adjust the color tone of the inks. As the

coloring material used in this case, a coloring material soluble in water is preferred from the viewpoint of stability of the resulting ink. When the water fastness of a recorded article formed by the ink according to the present invention is taken into consideration, a coloring material (direct dye) directly coloring a recording medium is preferably used. A coloring material having an azo group in its structure is more preferred. As the coloring material exhibiting no fluorescence properties, is preferably used a coloring material having a carboxyl group or its salt group in the structure thereof. A coloring material having only a carboxyl group or its salt group as a hydrophilic group of the coloring material is more preferred for use. Since the carboxyl group is weak in affinity for water compared with a sulfonic group, the water fastness of the recorded article formed by the ink according to the present invention can be improved.

[0041]

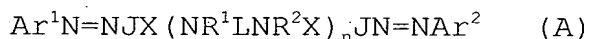
The content of the coloring material exhibiting no fluorescence properties in the inks according to this invention is preferably not lower than the content of the coloring material exhibiting fluorescence properties as described above. When an ink is made up in such a manner, a recorded state tends to remain even when the coloring material exhibiting fluorescence properties is lacking of water resistance, and fluorescence is lost by contact of the recorded article with water, so that it is prevented to completely lose the details recorded. However, when the

coloring material exhibiting no fluorescence properties is selected, it is required to suitably select the coloring material exhibiting no fluorescence properties according to the developed state of fluorescence properties in a recorded article, or balance with the coloring ability thereof.

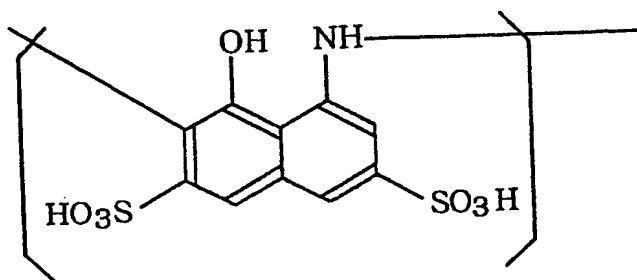
[0042]

Specific examples of the coloring material exhibiting no fluorescence properties include Direct Black 168, Direct Black 154, Direct Yellow 145, Direct Yellow 86, Direct Red 227, Direct Blue 199 and coloring materials represented by the following general formulae (A) and (B) in the form of a free acid. However, the present invention is not limited to these coloring materials.

[0043]



wherein J is the following formula

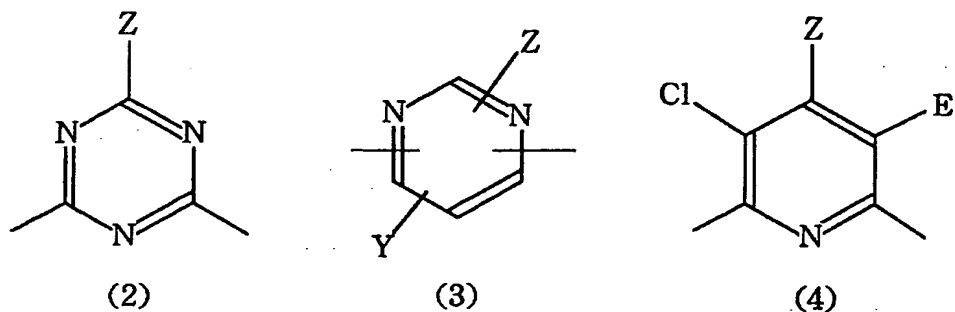


[0044]

Ar^1 and Ar^2 are, independently of each other, an aryl group or substituted aryl group, at least one of Ar^1 and Ar^2 is a substituted aryl group having at least one substituent

selected from COOH and COSH, R^1 and R^2 are, independently of each other, H, alkyl group, substituted alkyl group, alkenyl group, or substituted alkenyl group, L is a divalent organic linking group, n is 0 or 1, and X is a carbonyl group or a group represented by the following formulas (2) to (4):

[0045]



[0046]

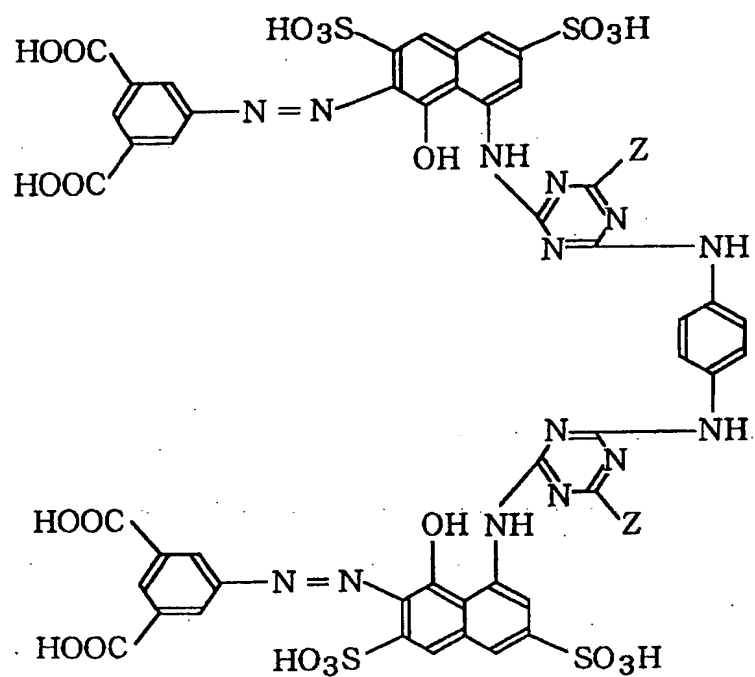
wherein Z in each of the formulae (2) to (4) is NR^3R^4 , SR^5 or OR^5 , Y in the formula (3) is H, Cl, Z, SR^6 or OR^6 , E in the formula (4) is Cl or CN, R^4 , R^5 , R^6 and R^7 are, independently of one another, H, alkyl group, substituted alkyl group, alkenyl group, substituted alkenyl group, aryl group, substituted aryl group, aralkyl group, or substituted aralkyl group, or R^4 and R^5 may be form a 5- or 6-membered ring together with nitrogen, with the proviso that the compounds represented by the general formula (A) have at least the same number of groups selected from COOH and COSH as SO_3H .

[0047]

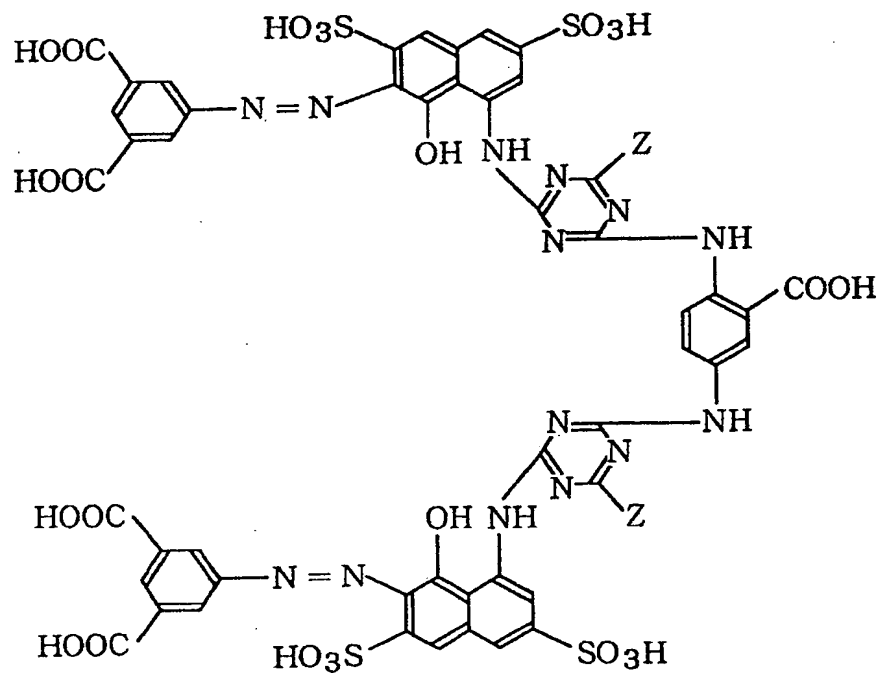
Examples of the compounds represented by the general formula (A) includes the followings:

[0048]

Exemplified Coloring Material (2):

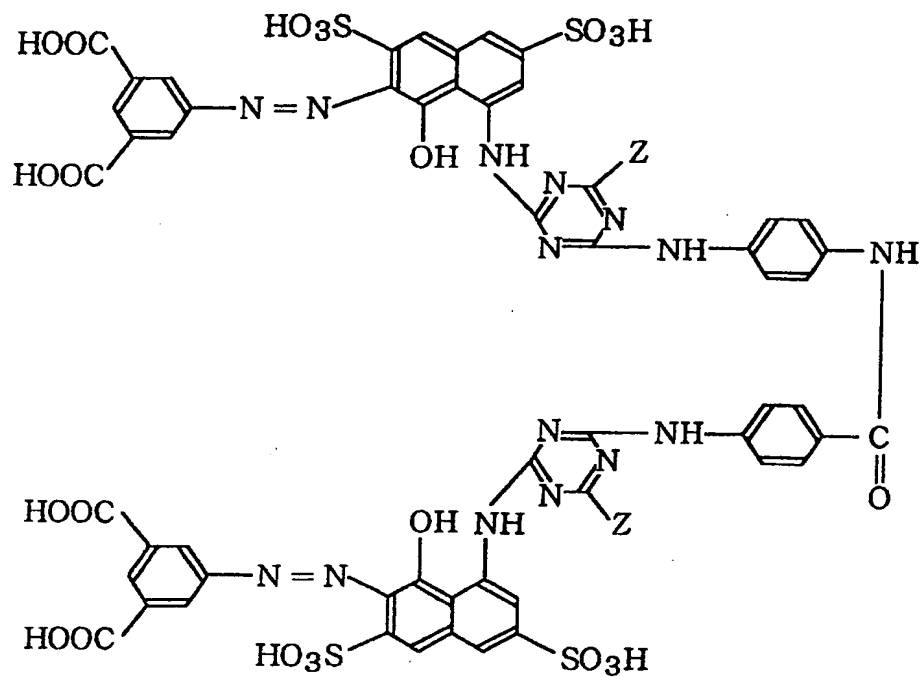


Exemplified Coloring Material (3):

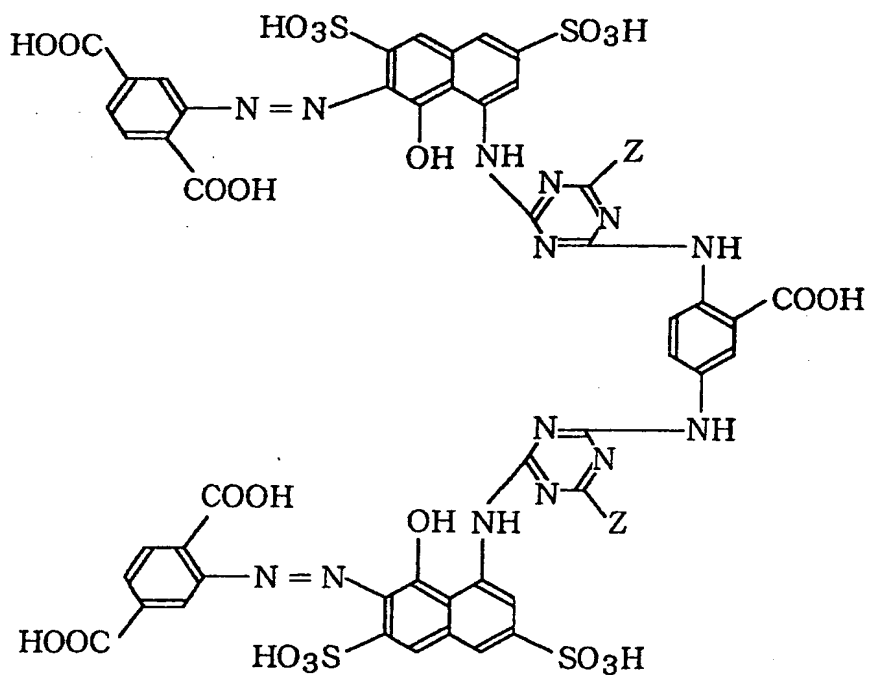


[0049]

Exemplified Coloring Material (4):

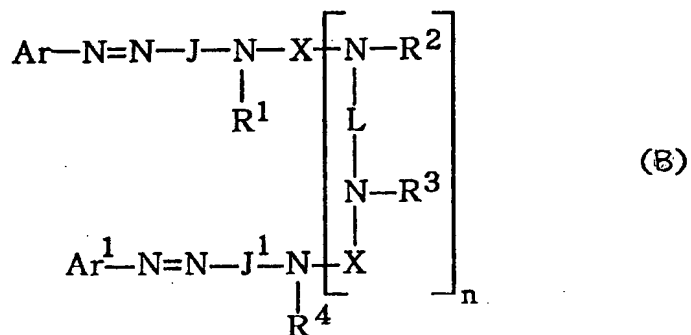


Exemplified Coloring Material (5):



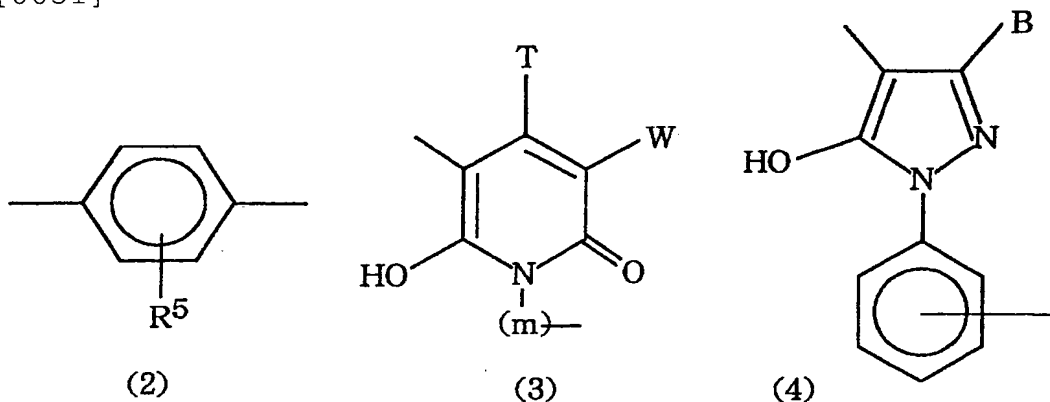
[0050]

Coloring material represented by the general formula (B) in the form of a free acid:



wherein Ar and Ar¹ are, independently of each other, an aryl group or substituted aryl group, at least one of Ar and Ar¹ is a substituted aryl group having a substituent selected from the group consisting of sulfonic, carboxyl and thiocarboxyl groups, J and J¹ are, independently of each other, a group represented by the following formula (2), (3) or (4):

[0051]



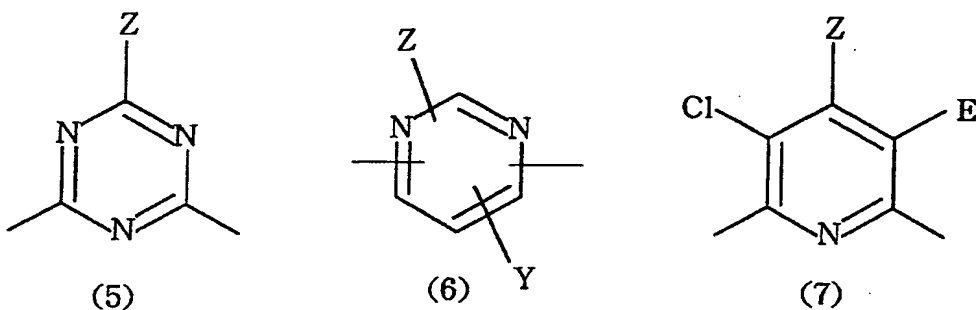
[0052]

wherein R⁵ in the formula (2) is selected from hydrogen,

alkyl groups, substituted alkyl groups, alkoxy groups, halogen, CN, ureide group and NHCOR^6 (R^6 being selected from hydrogen, alkyl groups, substituted alkyl groups, aryl groups, substituted aryl groups, aralkyl groups, and substituted aralkyl group, T in the formula (3) is an alkyl group, W is selected from hydrogen, $\text{CN CONR}^{10}\text{R}^{11}$, pyridinium group and carboxyl group, (R^{10} and R^{11} being, independently of each other, selected from hydrogen, alkyl groups and substituted alkyl groups, m is an alkylene group having 2 to 8 carbon atoms, and B in the formula (4) is selected from hydrogen, alkyl groups and carboxy group.

R^4 , R^5 , R^6 and R^7 in the formula (B) are, independently of one another, selected from H, alkyl groups and substituted alkyl groups, L is a divalent organic linking group, n is 0 or 1, and X is independently a carbonyl group or a group represented by the following formula (5), (6) or (7):

[0053]



wherein Z in each of the formulae (5) to (7) is selected from OR^7 , SR^7 and NR^8R^9 , Y is selected from hydrogen, Cl and Z, E is selected from Cl and CN, R^7 , R^8 and R^9 are, independently of one another, hydrogen, alkenyl group,

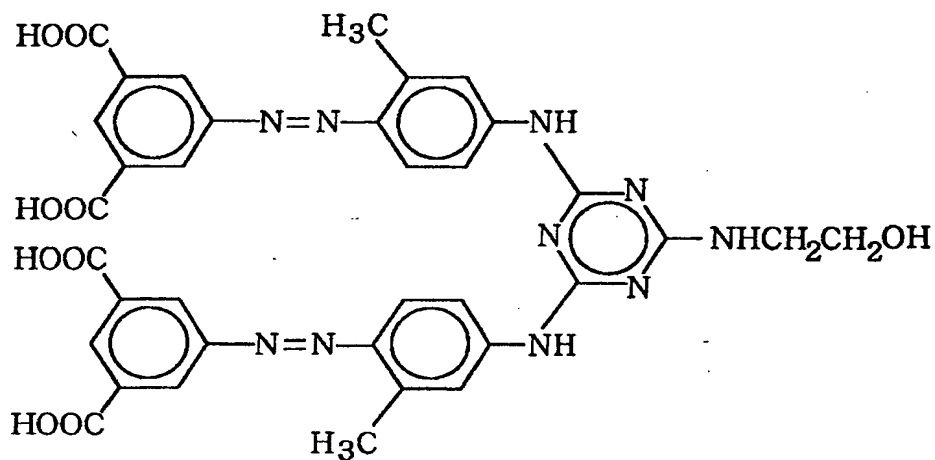
substituted alkenyl group, alkyl group, substituted alkyl group, aryl group, substituted aryl group, aralkyl group, or substituted aralkyl group, or R^8 and R^9 may be form a 5- or 6-membered ring together with nitrogen, with the proviso that when the compounds of the general formula (B) have no sulfonic group, the compounds have at least 2 groups selected from carboxyl and thiocarboxyl groups, or the compounds of the general formula (B) have at least the same number of groups selected from carboxyl and thiocarboxyl groups as the sulfonic group.

[0054]

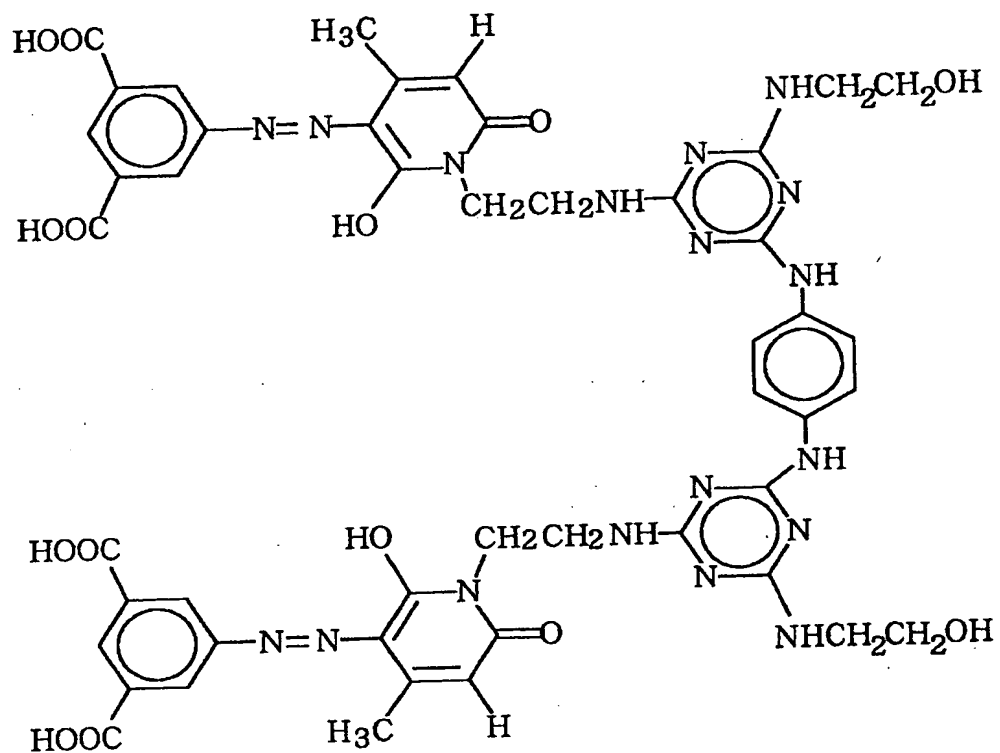
Examples of the compounds represented by the general formula (B) includes:

[0055]

Exemplified Coloring Material (6):

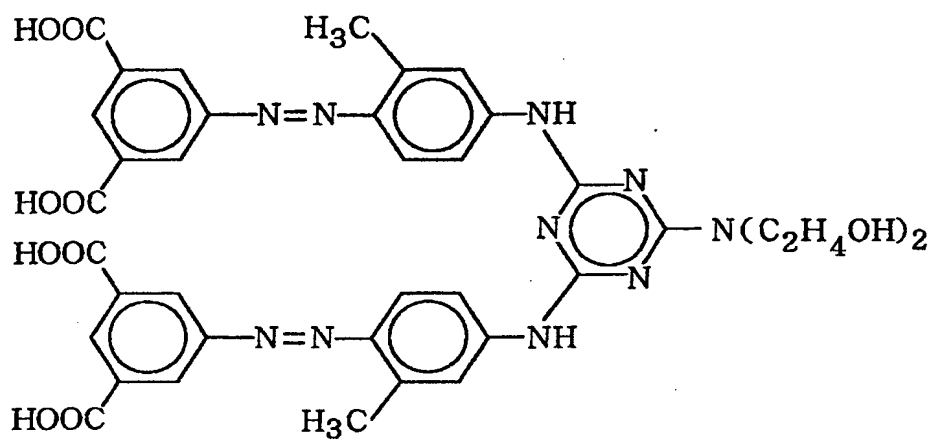


Exemplified Coloring Material (7):



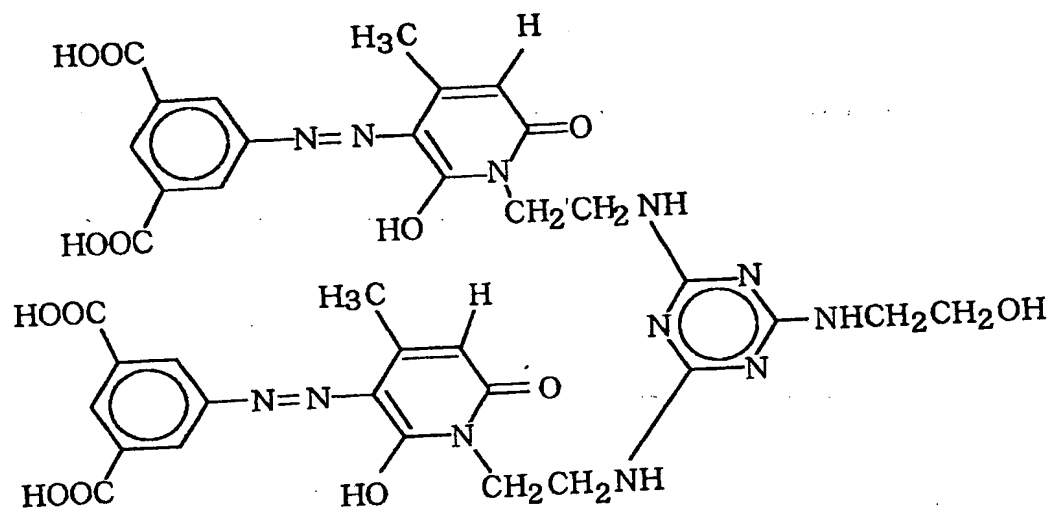
[0056]

Exemplified Coloring Material (8):

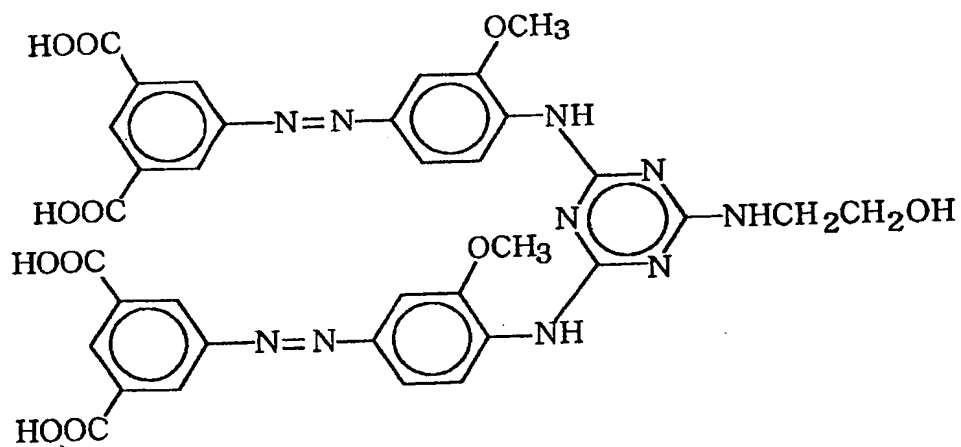


Exemplified

Coloring Material (9):

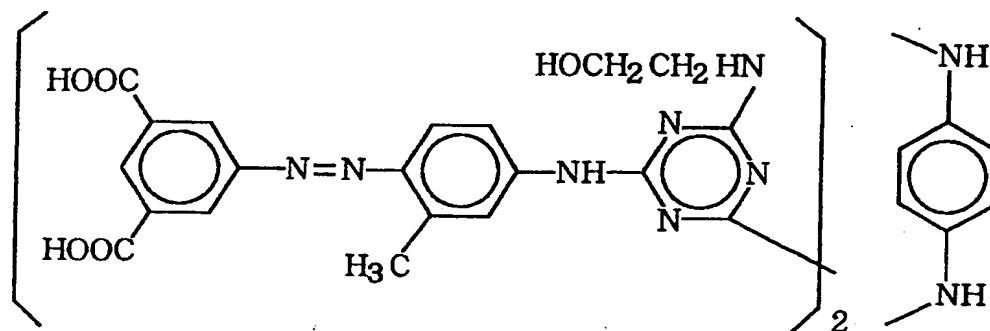


Exemplified Coloring Material (10):



[0057]

Exemplified Coloring Material (11):



[0058]

No particular limitation is imposed on the amount of such coloring material exhibiting no fluorescence properties as described above to be used. However, it is generally within a range of preferably from 0.1 to 15 % by weight, more preferably from 0.1 to 10 % by weight based on the total weight of the ink.

[0059]

For example, the inks according to this invention preferably have a surface tension of at most 40 mN/m (dyn/cm) because in order to develop the above-described mechanism, it is preferred from the viewpoint of development of the effect that for example, an ink droplet spreads after recording. Further, the pH of the inks according to this

embodiment is preferably at least 8 from the viewpoint of stability of the inks.

[0060]

In the inks according to this invention, it is preferred that an alkali metal ion and an ammonium ion be used in combination as counter ions to these coloring materials. When both ions are used in combination, the stability and ejection stability of the resulting ink are improved when the ink is used in ink-jet recording. As examples of the alkali metal ion, may be mentioned Li^+ , Na^+ and K^+ .

[0061]

In the inks according to this invention, it is preferred from the viewpoint of increasing the fluorescence intensity that the fluorescent coloring material be contained in at least a concentration sufficient to exhibit the maximum fluorescence intensity in the inks. Inferentially, the reason for it is considered to be due to the fact that since the apparent concentration of a coloring material is lowered by feathering or bleeding, penetration and the like of an ink when recording is conducted with such an ink on a recording medium, good coloring is retained on a selected recording medium when recording is conducted on the recording medium with the ink made up in such a manner.

[0062]

The fluorescent inks according to this invention made up in the above-described manner may also be used as

inks for general writing utensils, but are particularly effective when used in ink-jet recording. Ink-jet recording methods include a recording method in which mechanical energy is applied to an ink to eject droplets of the ink, and a recording method in which thermal energy is applied to an ink to eject droplets of the ink by bubbling of the ink. The inks according to this invention are particularly suitable for use in an ink-jet recording method of a type that an ink is ejected by the bubbling phenomenon of the ink caused by thermal energy. This recording method has a feature that the ejection of the ink becomes extremely stable, and no satellite dots generate. In this case, however, the thermal properties (for example, specific heat, coefficient of thermal expansion, heat conductivity, etc.) of the inks may be controlled in some cases.

[0063]

The ink according to the present invention solves the problem of durability of the ink on a printed or recorded article when the recording is effected on plain paper. At the same time, from the viewpoint of making the matching of the inks with an ink-jet head good, the inks according to this invention may desirably be controlled so as to have, as their own physical properties at 25°C, a surface tension of 30 to 40 mN/m (dyn/cm) and a viscosity of 15 cP or lower, preferably 10 cP or lower, more preferably 5 cP or lower. In order to control the inks to the above physical property values to solve problems in plain paper, the amount of water

contained in the inks according to this invention is preferably controlled to not less than 50 % by weight, but not more than 98 % by weight, more preferably not less than 60 % by weight, but not more than 95 % by weight.

[0064]

As a preferred method and an apparatus for conducting recording by using the inks according to the present invention, may be mentioned a method and an apparatus in which thermal energy corresponding to recording signals is applied to an ink within a recording head, and ink droplets are generated by the thermal energy.

[0065]

Examples of the construction of a head, which is a main component of such an apparatus, are illustrated in Figs. 1, 2 and 3. The head 13 is formed by bonding a glass, ceramic, silicon or plastic plate or the like having a groove 14 through which an ink is passed, to a heating head 15 which is used for thermal recording (the drawings show a head to which, however, the invention is not limited). The heating head 15 is composed of a protective film 16 made of silicon oxide or the like, aluminum electrodes 17-1 and 17-2, a heating resistor layer 18 made of nichrome or the like, a heat accumulating layer 19, and a substrate 20 made of alumina or the like having a good heat radiating property. An ink 21 comes up to an ejection orifice (a minute opening) 22 and forms a meniscus 23 due to a pressure P.

[0066]

Now, upon application of electric signals to the

electrodes 17-1 and 17-2, the heating head 15 rapidly generates heat at the region shown by "n" to form bubbles in the ink 21 which is in contact with this region. The meniscus 23 of the ink is projected by the pressure thus produced, and the ink 21 is ejected in the form of ink droplets 24 from the ejection orifice 22 toward a recording medium 25.

[0067]

Fig. 3 illustrates an appearance of a multi-head composed of an array of a number of heads as shown in Fig. 1. The multi-head is formed by closely bonding a glass plate 27 having a number of grooves 26 to a heating head 28 similar to that described in Fig. 1. Fig. 1 is a cross-sectional view of a head 13 taken along the flow path of ink, and Fig. 2 is a cross-sectional view taken along line A-B in Fig. 1.

[0068]

Fig. 4 illustrates an example of an ink-jet recording apparatus in which such a head as described above has been incorporated. In Fig. 4, reference numeral 61 designates a blade serving as a wiping member, one end of which is a stationary end held by a blade-holding member to form a cantilever. The blade 61 is provided at a position adjacent to a region in which a recording head 65 operates, and in this case shown in Fig. 4, is held in such a form that it protrudes into the course through which the recording head 65 is moved. Reference numeral 62 indicates a cap for the face of ejection openings of the recording

head 65, which is provided at a home position adjacent to the blade 61, and is so constructed that it moves in a direction perpendicular to a direction in which the recording head 65 is moved, and comes into contact with the face of ejection openings to cap it.

[0069]

Reference numeral 63 denotes an ink absorbing member provided adjoining to the blade 61 and, similar to the blade 61, held in such a form that it protrudes into the course through which the recording head 65 is moved. The above-described blade 61, cap 62 and ink absorbing member 63 constitute an ejection-recovery portion 64, where the blade 61 and ink absorbing member 63 remove water, dust and/or the like from the face of the ink-ejecting openings.

[0070]

Reference numeral 65 designates the recording head having an ejection-energy-generating means and serving to eject the ink onto a recording medium set in an opposing relation to the ejection opening face provided with the ejection openings to conduct recording. Reference numeral 66 indicates a carriage on which the recording head 65 is mounted so that the recording head 65 can be moved. The carriage 66 is slidably interlocked with a guide shaft 67 and is connected (not illustrated) at its part to a belt 69 driven by a motor 68. Thus, the carriage 66 can be moved along the guide shaft 67 and hence, the recording head 65 can be moved from a recording region to a region adjacent thereto.

[0071]

Reference numerals 51 and 52 denote a feeding part from which the recording medium is inserted, and feed rollers driven by a motor (not illustrated), respectively. With such a construction, the recording medium is fed to the position opposite to the ejection opening face of the recording head 65, and discharged from a discharge section provided with discharge rollers 53 with the progress of recording.

[0072]

In the above construction, the cap 62 in the ejection-recovery portion 64 is retracted from the path of motion of the recording head 65 when the recording head 65 is returned to its home position after completion of recording, and the blade 61 remains protruded into the path of motion. As a result, the ejection opening face of the recording head 65 is wiped. When the cap 62 comes into contact with the ejection opening face of the recording head 65 to cap it, the cap 62 is moved so as to protrude into the path of motion of the recording head 65.

[0073]

When the recording head 65 is moved from its home position to the position at which recording is started, the cap 62 and the blade 61 are at the same positions as the positions for the wiping as described above. As a result, the ejection opening face of the recording head 65 is also wiped at the time of this movement.

The above movement of the recording head to its home

position is made not only when the recording is completed or the recording head is recovered for ejection, but also when the recording head is moved between recording regions for the purpose of recording, during which it is moved to the home position adjacent to each recording region at given intervals, where the ejection opening face is wiped in accordance with this movement.

[0074]

Fig. 5 illustrates an exemplary ink cartridge in which an ink to be fed to a head through a member for feeding the ink, for example, a tube is contained. Here, reference numeral 40 designates an ink container containing the ink to be fed, as exemplified by a bag for ink. One end thereof is provided with a stopper 42 made of rubber. A needle (not illustrated) may be inserted into this stopper 42 so that the ink in the bag 40 for ink can be fed to the head. Reference numeral 44 indicates an ink absorbing member for receiving a waste ink. It is preferred that the ink container 40 be formed of a polyolefin, in particular, polyethylene, at its surface with which the ink comes into contact. The ink-jet recording apparatus according to the present invention are not limited to the apparatus as described above in which the head and the ink cartridge are separately provided. Therefore, a device in which these members are integrally formed as shown in Fig. 6 can also be preferably used.

[0075]

In Fig. 6, reference numeral 70 designates a

recording unit, in the interior of which an ink container containing an ink, for example, an ink holding member, is contained. The recording unit 70 is so constructed that the ink in such an ink holding member is ejected in the form of ink droplets through a head portion 71 having a plurality of orifices. In the present invention, polyurethane, cellulose, polyvinyl acetate, polyolefin or a polymer formed by inorganic compound(s) is preferably used as a material for the ink holding member. Further, an ink holding member composed of a porous material or having a multi-layer structure is preferably used. It is preferred that an ink holding member the direction of the multi-layer arrangement of the multi-layer structure of which is aligned in an ink discharging direction of the ink container be used. It is also preferred that an ink holding member having a contact surface with the ink container be used. Reference numeral 72 indicates an air passage for communicating the interior of the recording unit 70 with the atmosphere. This recording unit 70 is used in place of the recording head 65 shown in Fig. 4, and is detachably installed on the carriage 66.

[0076]

Other specific examples of the recording apparatus and recording heads preferably used in the present invention will hereinafter be described.

Fig. 12 is a schematic perspective view illustrating principal parts of a liquid-ejecting head of an ejection system that a bubble communicates with the

atmosphere upon ejection, and an exemplary ink-jet printer as a liquid-ejecting apparatus using this liquid-ejecting head. The ink-jet printer shown in Fig. 12 comprises a conveying device 1030 for intermittently conveying paper 1028 as a recording medium provided along the longitudinal direction in a casing 1008 in a direction shown by an arrow P in Fig. 12, a recording part 1010 reciprocatingly moved along a guide shaft 1014 in a direction of an arrow S substantially perpendicular to the conveying direction P of the paper 1028 by the conveying device 1030, and a driving part 1006 for movement as a driving means for reciprocatingly moving the recording part 1010. [0077]

The conveying device 1030 comprises a pair of roller units 1022a and 1022b and a pair of roller units 1024a and 1024b arranged in substantial parallel with and in opposed relation to each other, and a driving part 1020 for driving these respective roller units. By this construction, the paper 1028 is intermittently conveyed in a state that it is held between the respective roller units 1022a and 1022b and the roller units 1024a and 1024b in a direction shown by the arrow P in Fig. 12 when the driving part 1020 of the conveying device 1030 is operated.

[0078]

The driving part 1006 for movement comprises a belt 1016 wound around pulleys 1026a and 1026b respectively provided on rotating shafts oppositely arranged at a prescribed interval and a motor 1018 for driving the belt

1016 joined to a carriage member 1010a of the recording part 1010 arranged in substantial parallel to the roller units 1022a and 1022b in forward and reverse directions. [0079]

When the motor 1018 is operated to rotate the belt 1016 in a direction shown by an arrow R in Fig. 12, the carriage member 1010a of the recording part 1010 is moved by the prescribed movement in the direction shown by the arrow S in Fig. 12. When the motor 1018 is operated to rotate the belt 1016 in a direction reverse to the direction shown by the arrow R in Fig. 12, the carriage member 1010a of the recording part 1010 is moved by the prescribed movement in a direction reverse to the direction shown by the arrow S in Fig. 12. At an end of the driving part 1006 for movement, a recovery unit 1026 for conducting an ejection-recovery operation for the recording part 1010 is provided in opposed relation to an array of ink-ejection openings of the recording part 1010 at the home position of the carriage member 1010a.

[0080]

In the recording part 1010, ink-jet cartridges (hereinafter may be referred merely to as "cartridges" in some cases) 1012Y, 1012M, 1012C and 1012B for respective colors, for example, yellow, magenta, cyan and black, are detachably mounted on a carriage member 1010a.

[0081]

Fig. 13 illustrates an exemplary ink-jet cartridge capable of being mounted on the above-described ink-jet

recording apparatus. The cartridge 1012 in this embodiment is of a serial type, and its principal part is constructed by an ink-jet recording head 100 and a liquid tank 1001 for containing a liquid such as an ink. In the ink-jet recording head 100, a great number of ejection openings 832 for ejecting the liquid are formed, and the liquid such as an ink is directed to a common liquid chamber (see Fig. 14) in the liquid-ejecting head 100 through a liquid feed passage (not illustrated) from the liquid tank 1001. The cartridge 1012 shown in Fig. 13 is so constructed that the ink-jet recording head 100 and the liquid tank 1001 are integrally formed, and the liquid can be supplied to the interior of the liquid tank 1001 as needed. However, a structure that the liquid tank 1001 is replaceably joined to this liquid-ejecting head 100 may also be adopted.

[0082]

A specific example of the above-described liquid-ejecting head capable of being mounted on the ink-jet printer of such a construction will hereinafter be described in detail.

Fig. 14 is a schematic perspective view typically illustrating principal parts of a liquid-ejecting head which shows a basic embodiment of the present invention, and Figs. 15 to 18 are front views illustrating the form of ejection openings of the liquid-ejecting head shown in Fig. 14. Incidentally, in these drawings, electrical wiring and the like for driving electrothermal conversion elements are omitted.

[0083]

In the liquid-ejecting head according to this embodiment, such a substrate 934 composed of glass, ceramic, plastic or metal as illustrated in, for example, Fig. 14 is used. The material of such a substrate is not essential to the present invention and is not particularly limited so far as it functions as a part of a flow-path forming member and as a support for an ink ejection-energy-generating element, and a material layer for forming a liquid flow path and ejection openings, which will be described subsequently. Therefore, in this embodiment, the description is given in the case where an Si substrate (wafer) is used. Processes for the ejection openings include a forming process by laser beam, and a process in which for example, a photosensitive resin is used as an orifice plate (ejection-opening plate) 935, which will be described subsequently, to form ejection openings by an aligner such as MPA (mirror projection aligner).

[0084]

In Fig. 14, reference numeral 934 indicates a substrate equipped with electrothermal conversion elements (hereinafter may be referred as "heater" in some cases) 931 and an ink feed opening 933 formed of a long-grooved through-opening as a common liquid chamber. The heaters 931, which are thermal energy-generating means, are arranged in a zigzag form in a row on both sides of the ink feed opening 933 along the longitudinal direction thereof with an interval of, for example, 300 dpi between the electrothermal

conversion elements. Walls 936 for ink flow path for forming ink flow paths are provided on the substrate 934. Further, an ejection-opening plate 935 equipped with ejection openings 832 is provided on the walls 936 for ink flow path.

[0085]

In Fig. 14, the walls 936 for ink flow path and the ejection-opening plate 935 are illustrated as separate members. However, the walls 936 for ink flow path may be formed on the substrate 934 by a method such as spin coating, thereby forming the walls 936 for ink flow path and the ejection-opening plate 935 as the same member at the same time. In this embodiment, the side of the ejection-opening face (upper surface) 935a is subjected to a water-repellent treatment.

[0086]

In this example, the above-described head of the serial type that recording is conducted while scanning in the direction shown by the arrow S in Fig. 12 is used to conduct recording at, for example, 1,200 dpi. Driving frequency is 10 kHz, and ejection is conducted at the shortest time interval of 100 μ s in one ejection opening. As an example of dimensions of the head, a partition wall 936a for isolating adjacent nozzles from each other from the viewpoint of fluid has a width w of 14 μ m as illustrated in, for example, Fig. 15. As illustrated in Fig. 18, a bubbling chamber 1337 formed by the walls 936 for ink flow path has N_1 (width of the bubbling chamber) of 33 μ m and N_2

(length of the bubbling chamber) of 35 μm . The size of the heater 931 is 30 μm x 30 μm , the resistance value of the heater is 53 Ω , and driving voltage is 10.3 V. A head in which the heights of the wall 936 for ink flow path and the partition wall 936a are 12 μm , and the thickness of the ejection-opening plate is 11 μm may be used.

[0087]

In the section of an ejection opening part 940 provided in the ejection-opening plate including ejection openings 832, the form of a section taken along a direction intersecting the ejecting direction (thickness-wise direction of the orifice plate 935) of the ink is a substantially star form as illustrated in Fig. 16 and is generally formed by 6 projected portions 832a having a corner of an obtuse angle and 6 recessed portions 832b alternately arranged between these projected portions 832a and having a corner of an acute angle. More specifically, 6 grooves are formed in the thickness-wise direction (ejecting direction of the liquid) of the orifice plate shown in Fig. 14 by using the recessed portion 832b locally distant from the center O of the ejection opening as a top thereof and the projected portion 832a adjacent to this region and locally near from the center O of the ejection opening as a base (see Fig. 16).

[0088]

In the liquid-ejecting head illustrated, the ejection opening part 940 is such that, for example, a section taken along a direction intersecting the

thickness-wise direction thereof is in a form with 2 equilateral triangle having a side of $27\text{ }\mu\text{m}$ combined with each other in a state that one of them has been turned by 60 degrees. T_1 shown in Fig. 16 is $8\text{ }\mu\text{m}$. The angles of the projected portions 832a are all 120 degrees, while the angles of the recessed portions 832b are all 60 degrees. Accordingly, the center O of the ejection opening consists with the center of gravity G of a polygon formed by connecting centers (center (center of gravity) of a figure formed by connecting the top of the groove and 2 bases adjacent to the top) of the grooves adjacent to each other. The opening area of the ejection opening 832 in this embodiment is $400\text{ }\mu\text{m}^2$, and the opening area (area of the figure formed by connecting the top of the groove and 2 bases adjacent to the top) of the groove is about $33\text{ }\mu\text{m}^2$ per groove. Fig. 17 is a typical drawing illustrating a state that an ink has attached to the ejection opening portion shown in Fig. 16.

[0089]

An ejecting operation of a liquid by the ink-jet recording head of the above-described construction will hereinafter be described with reference to Figs. 19 to 26. Figs. 19 to 26 are cross-sectional views for illustrating the ejecting operation of a liquid by the liquid-ejecting head shown in Figs. 15 to 19 and are cross-sectional views of the bubbling chamber 1337 shown in Fig. 17 taken along line 20-20. In this section, an end of the ejection opening part 940 shown in Fig. 14 in the thickness-wise direction of the orifice plate is the top 1141a of a groove 1141. Fig.

19 illustrates a state that a film-like bubble has been formed on the heater, and Figs. 20, 21, 22, 23, 24, 25 and 26 illustrate states after about 1 μ s from the state in Fig. 19, after about 2 μ s from the state in Fig. 19, after about 3 μ s from the state in Fig. 19, after about 4 μ s from the state in Fig. 19, after about 5 μ s from the state in Fig. 19, after about 6 μ s from the state in Fig. 19 and after about 7 μ s from the state in Fig. 19, respectively. Incidentally, in the following description, "drop" or "drop-in" does not mean drop in the so-called gravity direction, but means the movement in the direction of an electrothermal conversion element irrespective of the installing direction of a head.

[0090]

First, when a bubble 101 is first formed in a liquid flow path 1338 on a heater 931 by energizing the heater 931 on the basis of a recording signal or the like as illustrated in Fig. 19, the bubble 101 quickly volumetrically expands and grows during about 2 μ s as illustrated in Figs. 20 and 21. The height of the bubble 101 in the greatest volume exceeds the face 935a of an ejection opening. At this time, the pressure of the bubble decreases from one to several to one to several tens as high as the atmospheric pressure.

[0091]

At the time about 2 μ s have elapsed from the formation of the bubble, the volume of the bubble 101 turns from the greatest volume to decreased volume as described above, and at substantially the same time as this, the

formation of a meniscus 102 is started. The meniscus 102 also recedes, i.e., drops in the direction of the heater 931 as illustrated in Fig. 22. In this embodiment, the ejection opening part in the liquid-ejecting head illustrated has a plurality of grooves 1141 in a dispersed state, whereby capillary force acts in an opposite direction F_c to the receding direction F_m of the meniscus at the portion of the groove 1141 when the meniscus 102 recedes. As a result, the forms of the meniscus and a main droplet (hereinafter may be referred to as "liquid" or "ink" in some cases) I when the meniscus recedes are compensated so as to give substantially symmetrical forms to the center of the ejection opening even if some variation is observed in the state of the bubble 101 by some cause.

[0092]

In this embodiment, the dropping velocity of this meniscus 102 is faster than the contracting velocity of the bubble 101, so that the bubble 101 communicates with the atmosphere in the vicinity of the lower surface of the ejection opening 832 at the time about 4 μ s have elapsed from the formation of the bubble as illustrated in Fig. 23. At this time, the liquid (ink) in the vicinity of the central axis of the ejection opening 832 drops toward the heater 931 because the liquid (ink) is pulled back on the side of the heater 931 by the negative pressure of the bubble 101 before the communication with the atmosphere retains the velocity in the direction toward the heater 931 by virtue of inertia even after the communication with the atmosphere.

The liquid (ink) dropped toward the side of the heater 931 reaches the surface of the heater 931 at the time about 5 μ s have elapsed from the formation of the bubble as illustrated in Fig. 24, and spreads so as to cover the surface of the heater 931 as illustrated in Fig. 25.

[0093]

The liquid spread so as to cover the surface of the heater 931 as described above has a vector in a horizontal direction along the surface of the heater 931. However, a vector in a direction intersecting the surface of the heater 931, for example, vertical direction vanishes, so that the liquid intends to remain on the surface of the heater 931, thereby pulling a liquid located on the upper side than such a liquid, i.e., a liquid keeping a velocity vector in the ejecting direction, downward. Thereafter, a liquid portion I_b between the liquid spread on the surface of the heater 931 and the liquid (main droplet) located on the upper side becomes thin, and is broken in the center of the surface of the heater 931 at the time about 7 μ s have elapsed from the formation of the bubble as illustrated in Fig. 26, whereby the liquid is separated into a main droplet I_a keeping a velocity vector in the ejecting direction and a liquid I_c spread on the surface of the heater 931. The position of such separation is desirably the interior of the liquid flow path 1338, preferably a side closer to the electrothermal conversion element (heater) 931 than the ejection opening 832.

[0094]

The main droplet I_a is ejected from the central portion of the ejection opening 832 without deviation in the ejecting direction and ejection slippage and impacted at the prescribed position of a recording surface on a recording medium. The liquid I_c spread on the surface of the heater 931 is ejected as a satellite droplet following the main droplet up to now. However, it remains on the surface of the heater 931 without being ejected. Since the ejection of the satellite droplet can be prevented as described above, splash easy to occur by the ejection of the satellite droplet can be prevented, and staining of the recording surface on the recording medium with mist suspending in the form of fog can be surely prevented. In Figs. 23 to 21, reference characters I_a and I_c indicate an ink (ink within the groove) attached to the groove portion and an ink remaining in the liquid flow path, respectively.

[0095]

As described above, in the liquid-ejecting head illustrated, the direction of the main droplet upon ejection can be stabilized by the plural grooves dispersed to the center of the ejection opening when the liquid is ejected at the stage that the volume of the bubble decreases after growing into the greatest volume. As a result, a liquid-ejecting head free of slippage in the ejecting direction and high in impact accuracy can be provided. In addition, ejection can be stably conducted against the variation of bubbling at high driving frequency, whereby high-speed and high-definition printing can be realized.

[0096]

In particular, the liquid is ejected by communicating the bubble with the atmosphere for the first time at the stage that the volume of the bubble decreases, whereby mist occurred upon the ejection of the droplet by communicating the bubble with the atmosphere can be prevented, so that the state that droplets attach to the ejection opening face, which forms the main cause of the so-called sudden ejection failure, can also be inhibited. As another embodiment of the recording head of the ejection system that a bubble is communicated with the atmosphere upon ejection, may be mentioned the so-called edge shooter type as described in, for example, Japanese Patent Registration No. 2783647.

[0097]

In particular, the present invention has excellent effects in recording heads and recording apparatus of an ink-jet system that thermal energy is utilized to form a droplet to be ejected, thereby conducting recording, among the ink-jet recording systems.

[0098]

With respect to the typical construction and principle thereof, those using the basic principle disclosed in, for example, U.S. Patent Nos. 4,723,129 and 4,740,796 are preferred.

This system may be applied to any of the so-called On-Demand type and continuous type. In particular, the On-Demand type is effective because at least one driving

signal which corresponds to recording information and gives a rapid temperature rise exceeding film boiling is applied to an electrothermal converter arranged corresponding to a sheet or liquid path, in which a liquid (ink) is held, thereby causing the electrothermal converter to generate thermal energy to cause film boiling on the heat-acting surface of a recording head, so that a bubble can be formed in the liquid (ink) in response to the driving signal in relation of one to one. The liquid (ink) is ejected through an ejection opening by the growth-contraction of this bubble to form at least one droplet. When the driving signal is applied in the form of a pulse, the growth-contraction of the bubble is suitably conducted in a moment, so that the ejection of the liquid (ink) excellent in responsiveness in particular can be achieved. It is therefore preferable to use such pulsed signals.

[0099]

As the pulsed driving signal, such signals as described in U.S. Patent Nos. 4,463,359 and 4,345,262 are suitable. When the conditions described in U.S. Patent No. 4,313,124 that is an invention relating to the rate of temperature rise on the heat-acting surface are adopted, far excellent recording can be conducted.

[0100]

As the construction of the recording head, such combined constructions (linear liquid flow path or perpendicular liquid flow path) of ejection openings, a liquid flow path and electrothermal converters as disclosed

in the above-described U.S. specifications, and besides constructions based on U.S. Patent Nos. 4,558,333 and 4,459,600 which disclose the construction that a heat-acting portion is arranged in a curved region may also be preferably used.

[0101]

In addition, constructions based on Japanese Patent Application Laid-Open No. 59-123670 which discloses the construction that a slit common to a plurality of electrothermal converters are used as an ejection part of the electrothermal converters, and Japanese Patent Application Laid-Open No. 59-138461 which discloses the construction that an opening absorbing pressure wave of thermal energy is provided in opposition to an ejection part may also be effective for the present invention.

[0102]

Further, as a full-line type recording head having a length corresponding to the longest width of recording media, on which a recording apparatus can record, both construction that the length is met by such a combination of plural recording heads as disclosed in the above-described specifications and construction as one recording head integrally formed may be used, and the above-described effects of the present invention can be more effectively exhibited.

[0103]

In addition, the present invention is effective even when a replaceable, chip type recording head in which

electrical connection to an apparatus body and the feed of an ink from the apparatus body become feasible by installing in the apparatus body, or a cartridge type recording head in which an ink tank is provided integrally in a recording head itself is used.

[0104]

Further, the addition of recovery means for a recording head, preliminary auxiliary means, etc. which are provided as constitution of the recording apparatus according to the present invention is preferred because the effects of the present invention can be more stabilized. Specifically, capping means for the recording head, cleaning means, pressurizing or sucking means, preliminary heating means by electrothermal converters, other heating elements than these or combinations thereof, and preliminary ejection mode that ejection separate from recording is conducted may also be effective for stable recording.

[0105]

As a recording mode of the recording apparatus, the present invention is extremely effective for not only recording mode using main colors such as black, but also apparatus equipped with at least one of complex color of different colors and full color by color mixing by integrally constructing a recording head or combining plural recording heads with each other.

[0106]

In the above-described embodiments of the present

invention, the inks have been described as liquid. However, inks solidified at room temperature or lower may also be used so far as they are softened or liquid at room temperature, or exhibit a liquid phase upon application of recording signals used because it is general in the above-described ink-jet systems that the temperature control of an ink itself is conducted within a range of from 30 to 70°C to adjust the viscosity of the ink so as to fall within a stable ejection range.

[0107]

In addition, inks that are liquefied by applying thermal energy according to recording signals and ejected as liquid inks, such as inks that temperature rise by thermal energy is positively prevented by using the thermal energy as energy for phase change from a solid phase to a liquid phase and inks solidified in a state left to stand for the purpose of preventing evaporation of the inks, and inks of a nature that they are liquefied for the first time by thermal energy, such as those already beginning to solidify at the time they reach a recording medium, may also be applied to the present invention. In such a case, the inks may be in a form that they are opposed to electrothermal converters in a state retained as a liquid or solid in recesses or through-holes in a porous sheet as described in Japanese Patent Application Laid-Open No. 54-56847 or 60-71260. In the present invention, the above-described film boiling system is most effective for the above-described inks.

[0108]

Furthermore, as forms of the recording apparatus according to the present invention, forms that the apparatus is integrally or separately provided as an image output terminal for information processing instruments such as word processors and computers, and forms such as copying machines combined with a reader and facsimiles having a transmitting-receiving function may also be adopted.

[0109]

The outline of a liquid-ejecting apparatus in which the above-described liquid-ejecting head is installed will hereinafter be described.

Fig. 29 is a schematic perspective view of an ink-jet recording apparatus 600 which is an example of a liquid-ejecting apparatus to which the liquid-ejecting head described above can be installed and applied.

[0110]

In Fig. 29, an ink-jet head cartridge 601 is so constructed that the above-described liquid-ejecting head is integrally formed with an ink tank with an ink to be fed to the liquid-ejecting head held therein. The ink-jet head cartridge 601 is mounted on a carriage 607 engaged with a spiral groove 606 in a lead screw 605 rotating through driving force-transmitting gears 603 and 604 interlocking with the forward and reverse rotations of a driving motor 602 and reciprocatingly moved in directions shown by arrows a, b along a guide 608 together with the carriage 607 by the power of the driving motor 602. A recording medium P

is conveyed on a platen roller 609 by a recording medium-conveying means (not illustrated) and pressed against the platen roller 609 over the moving direction of the carriage 607 by a paper presser plate 610.

[0111]

Photocouplers 611 and 612 are arranged in the vicinity of an end of the lead screw 605. These are home position-detecting means for confirming the presence of a lever 607a of the carriage 607 in this region to conduct change-over of the rotating direction of the driving motor 602, and the like.

[0112]

A support member 613 serves to support a cap member 614 covering the front surface (ejection opening face) of the ink-jet head cartridge 601, in which ejection openings are present. An ink-sucking means 615 serves to suck an ink stored in the interior of the cap member 614 by empty ejection or the like from the ink-jet head cartridge 601. By this ink-sucking means 615, suction recovery of the ink-jet head cartridge 601 is conducted through an opening (not illustrated) in the cap. A cleaning blade 617 for wiping the ejection opening face of the ink-jet head cartridge 601 is provided movably in forward and backward directions (directions perpendicular to the moving directions of the carriage 607) by a moving member 618. These cleaning blade 617 and moving member 618 are supported by a body support 619. The cleaning blade 617 is not limited to this form, and any other well-known cleaning blade may be used.

[0113]

Upon the suction recovery operation of the liquid-ejecting head, a lever 620 for initiating suction is moved with the movement of a cam 621 engaged with the carriage 607, and the driving power from the driving motor 602 is transfer-controlled by a publicly known means such as clutch shift. An ink-jet recording control part for applying a signal to a heater provided in the liquid-ejecting head of the ink-jet head cartridge 601 and conducting drive control of the above-described respective mechanisms is provided on the side of the apparatus body and not illustrated here.

[0114]

The ink-jet recording apparatus 600 having the above-described construction conducts recording on the recording medium P' conveyed on the platen roller 609 by the recording medium-conveying means (not illustrated) while reciprocatingly moving the ink-jet head cartridge 601 over the full width of the recording medium P'.

[0115]

Preferred modes of the inks according to the present invention described above, and preferred modes of the ink-jet recording process using these inks, the recorded articles formed by the process, the recording unit, the ink-jet cartridge and the ink-jet recording apparatus will hereinafter be shown collectively.

[0116]

The inks according to the present invention have

a feature that they comprise the 2 organic compounds incompatible with each other, the fluorescent coloring material in the content of not more than 1. 5% by weight in the ink, glycol having a vapor pressure not higher than that of diethylene glycol, and the liquid medium dissolving or dispersing these materials therein. They are preferably water-based inks. In addition, the fluorescent coloring materials are preferably the coloring material dissolved or dispersed in water, and particularly, water-soluble dyes. Further, the content of the fluorescent coloring material is at least a concentration sufficient to exhibit the maximum fluorescence intensity in the inks, and particularly the content of the coloring material in the inks is at least a concentration sufficient to exhibit the maximum fluorescence intensity in the inks in a state dissolved in water. Specifically, the content of the fluorescent coloring material is preferably not more than 1. 0% by weight.

[0117]

As the 2 organic compounds incompatible with each other for making up the inks according to the present invention, it is preferred that one of the 2 organic compounds incompatible with each other has a solubility parameter of at least 15, and the other has a solubility parameter of at most 13, that the 2 organic compounds incompatible with each other are both nonpolar compounds, that the 2 organic compounds incompatible with each other are both water-soluble, that the 2 organic compounds

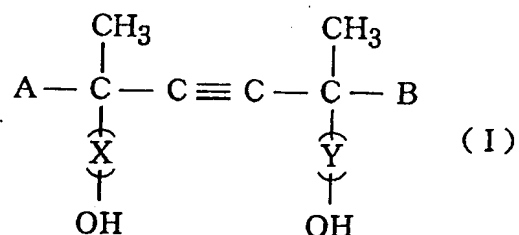
incompatible with each other are both liquid, that one of the 2 organic compounds incompatible with each other has a glycerol group, and that the organic compound having a glycerol group is a compound having at least 3 hydroxyl groups. The inks are preferably liquid at normal temperature.

[0118]

Further, it is preferable to use a nonionic surfactant as the other of the 2 organic compounds incompatible with each other. It is particularly preferred that the nonionic surfactant is liquid at normal temperature, or HLB of the nonionic surfactant is at most 13. It is also preferred that when the nonionic surfactant is contained in the inks, the nonionic surfactant is contained in the inks in an amount that the nonionic surfactant is not separated at an interface of an aqueous solution in a state of the aqueous solution, and the nonionic surfactant is not separated at an interface of the ink in a state of an ink from which the coloring material has been removed.

[0119]

Preferred modes of the inks according to the present invention include an ink that the nonionic surfactant making up the ink has an acetylene group, and an ink that the nonionic surfactant has a structure represented by the following general formula (I)



wherein A and B are, independently of each other, C_nH_{2n+1} (n being an integer of 1 to 10), and X and Y are, independently of each other, a ring-opening ethylene oxide unit and/or a ring-opening propylene oxide unit. Further, when such a nonionic surfactant as described above is contained in the ink, it is preferable that the content of the nonionic surfactant in the ink is not less than 1% by weight.

[0120]

Further preferred modes of the inks according to the present invention include an ink in which a monohydric alcohol is contained in addition to the above-described essential components, and an ink in which a coloring material exhibiting no fluorescence properties is additionally contained. The coloring material exhibiting no fluorescence properties used in this case is preferably a coloring material having a water-solubility. Further, the coloring material exhibiting no fluorescence properties is preferably a coloring material directly coloring a recording medium, more preferably an azo dye. As further preferred modes of the inks, may be mentioned an ink in which the content of the coloring material exhibiting no fluorescence properties in the inks is higher than the content of the fluorescent coloring material, an ink in which the coloring material exhibiting no fluorescence properties has a carboxyl group or its salt group, and an ink in which the hydrophilic group of the coloring material exhibiting no fluorescence properties has only a carboxyl

group or its salt group.

[0121]

Further preferred modes of the inks according to the present invention include an ink in which at least one selected from urea and urea derivatives is contained in addition to the above-described essential components, an ink in which the urea derivative is not a cyclic compound, and an ink in which the urea derivative is at least one selected from alkyl derivatives of urea and ethylene oxide and/or propylene oxide adducts of urea.

[0122]

The inks according to the present invention composed of such components as described above preferably is an ink which is nonionic in an ink system from which the coloring material and additives have been removed, have a surface tension of at most 40 mN/m (dyn/cm) and a pH of at least 8. Further, an ink in which an ammonium ion and an alkali metal ion are used in combination as counter ions of the coloring material(s) in the ink is preferred. Further, an ink in which the excitation maximum wavelength of the ink is smaller than the fluorescence maximum wavelength of the ink is preferred.

[0123]

The ink-jet recording process according to the present invention, in which an ink is ejected from an orifice in response to recording signals to conduct recording on a recording medium, thereby obtaining a recorded article features that the above-mentioned ink of a preferred mode

according to the present invention is used as said ink. The ink-jet recording process according to the present invention is preferably of the type that thermal energy is applied to an ink to be ejected from the orifice to eject droplets of the ink. Preferred modes of the present invention include a recorded article obtained by the above-described ink-jet recording process, wherein the fluorescence intensity of a recorded portion formed on wood-free paper has a relatively proportional relationship to the water content in the wood-free paper, and a recorded article in which the excitation maximum wavelength is smaller than the fluorescence maximum wavelength.

[0124]

Another preferred mode of the present invention includes a recording unit comprising an ink container containing the ink and a head portion for ejecting the ink as ink droplets, the ink used therein is preferably at least one of the inks according to the present invention having preferred embodiments described above. Preferable examples of the recording unit according to the present invention include a recording unit in which the head portion has a construction that thermal energy is applied to the ink to eject ink droplets, a recording unit in which the ink container is formed of a polyolefin, a recording unit in which the ink container has an ink holding member therein, a recording unit in which the ink holding member is formed of at least one selected from the group consisting of polyurethane, cellulose, polyvinyl acetate and polyolefin,

and a recording unit in which the ink holding member is composed of a polymer formed by inorganic compound(s).

[0125]

Further preferable examples of the recording unit according to the present invention include a recording unit in which the ink holding member is composed of a porous material, a recording unit in which the ink holding member has a multi-layer structure, a recording unit in which the direction of the multi-layer arrangement of the multi-layer structure is aligned in an ink discharging direction of the ink container, a recording unit in which the ink holding member is composed of fiber flocculate, a recording unit in which the fiber flocculate is oriented in an ink discharging direction of the ink container, and a recording unit in which the ink holding member has a contact surface with the ink container.

[0126]

A further preferred mode of the present invention includes an ink cartridge comprising an ink container containing the ink, which is at least one of the inks according to the present invention having preferred embodiments described above. Preferable examples of the recording unit according to the present invention include a recording unit in which the head portion has a construction that thermal energy is applied to the ink to eject ink droplets, a recording unit in which the ink container is formed of a polyolefin, a recording unit in which the ink container has an ink holding member therein, a recording

unit in which the ink holding member is formed of at least one selected from the group consisting of polyurethane, cellulose, polyvinyl acetate and polyolefin, and a recording unit in which the ink holding member is composed of a polymer formed by inorganic compound(s).

[0127]

Further preferable examples of the recording cartridge according to the present invention include an ink cartridge in which the ink holding member is composed of a porous material, an ink cartridge in which the ink holding member has a multi-layer structure, an ink cartridge in which the direction of the multi-layer arrangement of the multi-layer structure is aligned in an ink discharging direction of the ink container, an ink cartridge in which the ink holding member is composed of fiber flocculate, an ink cartridge in which the fiber flocculate is oriented in an ink discharging direction of the ink container, and an ink cartridge in which the ink holding member has a contact surface with the ink container.

[0128]

A still further preferred mode of the present invention includes an ink-jet recording apparatus comprising an ink container containing the ink and a head portion for ejecting the ink as ink droplets, the ink being at least one of the inks according to the present invention having the preferred embodiments described above. Preferable examples thereof include the recording unit which is at least one of the recording units of the present

invention described above.

[0129]

A yet still further preferred mode of the present invention includes an ink-jet recording apparatus equipped with the ink cartridge having a recording unit for ejecting ink droplets and an ink container containing the ink and the above-mentioned ink supply portion for supplying the ink from the ink cartridge to the recording head ink cartridge according to the present invention, the ink being at least one of the inks according to the present invention having the preferred embodiments described above. Preferable examples thereof include the recording unit which is at least one of the recording units of the present invention described above, and the ink cartridge which is at least one of the ink cartridges of the present invention described above.

[0130]

[Embodiments]

The present invention will hereinafter be described more specifically by the following Examples and Comparative Examples. Incidentally, all designations of "part" or "parts" and "%" as will be used in the following examples mean part or parts by weight and % by weight unless expressly noted.

EXAMPLES 1 to 7, and COMPARATIVE EXAMPLES 1 to 5:

Their corresponding components shown in Table 1 were mixed and thoroughly stirred into solutions or dispersions. The resultant solutions or dispersions were

separately filtered under pressure through a Fluoropore Filter (trade name; product of Sumitomo Electric Industries, Ltd.) having a pore size of 0.1 μm , thereby preparing inks according to EXAMPLES and COMPARATIVE EXAMPLES.

[0131]

[0132]

Table 1-2: Ink compositions of COMPARATIVE EXAMPLES

	COMPARATIVE					EXAMPLE
	1	2	3	4	5	
Compound exhibiting fluorescence properties or coloring material exhibiting fluorescence properties	C.I. Acid Red 52	0.3	0.3	0.3	0.3	0.4
	C.I. Acid Red 92				2.0	0.4
	C.I. Solvent Green 7					
Coloring material exhibiting no fluorescence properties	Exemplified Coloring material (11)				0.4	
	Exemplified Coloring material (2)					
	C.I. Direct Yellow 86		0.4			
Compound having glycerol group	Glycerol		10	10	10	10
	Glycerol (dimer)					
	Xylitol					
Glycol	Ethylene glycol	10			10	
	Diethylene glycol		10			10
	Triethylene glycol	10				10
	Tripropylene glycol					
	Surfynol 440					
Surfactant	Surfynol 465		2	2		2
	Surfynol 485					
	Exemplified Compound (V)					
	Exemplified Compound (II)					
	Sodium laurate	1				
Other component	Urea					
	Triethanolamine					2
	Isopropylalcohol	2		4	4	4
	Purified water					
					Balance	

[0133]

<Evaluation>

The resultant inks according to EXAMPLES and COMPARATIVE EXAMPLES were used to evaluate the inks by means of an ink-jet printer BJJ 800 (trade name, manufactured by Canon Inc.) in accordance with the following respective methods and standards. The results are shown in Table 2.

[0134]

(Evaluation of ejection stability)

Each of the inks was charged in a prescribed amount into an ink tank of BJJ 800 to record English characters and numerals on commercially available wood-free paper until the ink within the ink tank was used up. After the recording, recorded articles obtained at the first and the last of the recording were compared with each other to evaluate the ink as to the ejection stability in accordance with the following standard:

A: No difference was made between both recorded articles;

B: Some disorder in quality was observed in the recorded article obtained at the last of the recording;

C: Great disorder in quality was observed in the recorded article obtained at the last of the recording, and ejection failure was also marked.

[0135]

(Evaluation of stability)

Each of the resultant inks was placed in a laboratory

glass dish and left to stand for 7 days under an environment of 60°C. Thereafter, the condition of the ink was visually observed to evaluate the ink as to the stability in accordance with the following standard:

A: Neither precipitate nor separation of ink components was observed;

B: Separation was observed at an interface of the ink;

C: Precipitate was observed to a great extent.

[0136]

(Evaluation of shelf stability)

Each of the resultant inks was placed in a glass container, closed and left to stand for 1 month under an environment of 60°C. Thereafter, the ink was left to stand for additional 1 day under an environment of normal temperature and then visually observed to evaluate the ink as to the shelf stability in accordance with the following standard:

A: None of precipitate, suspended matter and separation of ink components were observed;

B: Precipitate or suspended matter was slightly observed;

C: Separation was observed at a gas-liquid interface of the ink;

D: Precipitate was observed to a great extent.

[0137]

(Evaluation of coloring ability)

English characters and numerals and a single-color

image were recorded on commercially available wood-free paper to visually observe the resultant printed article, thereby evaluating each ink sample as to the coloring ability in accordance with the following standard:

A: Bright or clear:

B: Not look dull though not bright;

C: Look dull.

[0138]

(Evaluation 1 of fluorescence properties)

A solid image was printed at 50% duty on commercially available wood-free paper under an environment of 23°C and 50% RH to measure fluorescence intensity of the resulting print at a excitation wavelength of 260 nm and a emission wavelength of 600 nm by means of a fluorescence intensity meter, FP-750 (manufactured by Nippon Keiko K.K.) under conditions that the fluorescence intensity of the coloring materials used in EXAMPLES AND COMPARATIVE EXAMPLES is easiest to measure, thereby evaluating the inks as to the fluorescence properties in accordance with the following standard:

A: Fluorescence intensity ≥ 350 ;

B: $350 > \text{Fluorescence intensity} \geq 300$;

C: $200 > \text{Fluorescence intensity}$.

[0139]

(Evaluation 2 of fluorescence properties)

The same measurement as in Evaluation 1 of fluorescence properties was conducted under low-temperature and low-humidity environment of 15°C and 10% RH

to evaluate the inks in accordance with the same method and standard as described above. The results are shown in Table 2.

[0140]

.(Change in fluorescence properties with time)

A solid image was printed at 50% duty on commercially available wood-free paper to measure fluorescence intensity of the resulting print by means of the fluorescence intensity meter, FP-750. The resultant solid printed sample was stuck on a wall in a room that was not directly exposed to sunlight and left to stand for 30 days in a state that a fluorescent lighting was turned on. Thereafter, the fluorescence intensity of the print was measured again. The resultant fluorescence intensity values were compared to evaluate the ink sample in accordance with the following standard:

A: Percent reduction of fluorescence intensity was not more than 5%;

B: Percent reduction of fluorescence intensity was not more than 10%;

C: Percent reduction of fluorescence intensity was more than 10%.

[0141]

Table 2: Evaluation results of EXAMPLES and COMPARATIVE
EXAMPLES

	Example								Comp. example						
	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7
Ejection stability	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Stability	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Shelf stability	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Coloring ability	A	A	A	A	A	A	A	A	C	C	A	C	C	C	C
Fluorescence 1	A	A	A	A	A	A	A	A	C	C	A	C	C	C	C
Fluorescence 2	A	A	A	A	A	A	A	A	C	C	B	C	C	C	C

[0142]

[Effect of the Invention]

As described above, according to the present invention, there can be provided an ink which can provide a recorded article to the recorded portion of which, by fully making good use of the fluorescence properties of the ink, the recorded article is excellent in print quality including coloring ability, said ink being capable of enhancing the stability and reliability of the recorded article, an ink-jet recording process using such an ink, a recorded article obtained by the recording process, and instruments using such an ink. Also, according to the present invention, there can also be provided the ink with which can effectively suppress the deteriorated of the fluorescence intensity of

a recorded article with time, an ink-jet recording process using such an ink, a recorded article obtained by the recording process, and instruments using such an ink.

[Brief Description of the Drawings]

[Figure 1]

A longitudinal cross-sectional view of a head of an ink-jet recording apparatus.

[Figure 2]

A transverse cross-sectional view of the head of the ink-jet recording apparatus.

[Figure 3]

A perspective view of the appearance of a multi-head which is an array of such heads as shown in Fig. 1.

[Figure 4]

A perspective view illustrating an exemplary ink-jet recording apparatus.

[Figure 5]

A longitudinal cross-sectional view of an ink cartridge.

[Figure 6]

A perspective view illustrating an exemplary recording unit.

[Figure 7]

A perspective view illustrating an exemplary recording unit.

[Figure 8]

A view illustrating the mechanism of coloring including fluorescence intensity according to the present

invention.

[Figure 9]

A view illustrating the mechanism of coloring including fluorescence intensity according to the present invention.

[Figure 10]

A view illustrating the mechanism of coloring including fluorescence intensity according to the present invention.

[Figure 11]

A view illustrating the mechanism of coloring including fluorescence intensity according to the present invention.

[Figure 12]

A schematic perspective view illustrating principal parts in an exemplary ink-jet printer capable of installing a liquid-ejecting head.

[Figure 13]

A schematic perspective view illustrating an exemplary ink-jet cartridge equipped with the liquid-ejecting head.

[Figure 14]

A schematic perspective view typically illustrating principal parts of an exemplary liquid-ejecting head.

[Figure 15]

A conceptual view illustrating a part extracted from the exemplary liquid-ejecting head.

[Figure 16]

An enlarged view illustrating a part of the ejection openings shown in Fig. 15.

[Figure 17]

A view typically illustrating a state that an ink has attached to the ejection opening portion shown in Fig. 16.

[Figure 18]

A view typically illustrating a principal part in Fig. 15.

[Figure 19]

A schematic cross-sectional view corresponding to a sectional form taken along line X-X in Fig. 18 and illustrating an ejecting operation of a liquid in the liquid-ejecting head with time together with Figs. 20 to 26.

[Figure 20]

A schematic cross-sectional view corresponding to a sectional form taken along line X-X in Fig. 18 and illustrating an ejecting operation of the liquid in the liquid-ejecting head with time together with Figs. 19 and 21 to 26.

[Figure 21]

A schematic cross-sectional view corresponding to a sectional form taken along line X-x in Fig. 18 and illustrating an ejecting operation of the liquid in the liquid-ejecting head with time together with Figs. 19, 20 and 22 to 26.

[Figure 22]

A schematic cross-sectional view corresponding to a sectional form taken along line X-X in Fig. 18 in the liquid-ejecting head and illustrating an ejecting operation of the liquid in the liquid-ejecting head with time together with Figs. 19 to 21 and 23 to 26.

[Figure 23]

A schematic cross-sectional view corresponding to a sectional form taken along line X-X in Fig. 18 and illustrating an ejecting operation of the liquid in the liquid-ejecting head with time together with Figs. 19 to 22 and 24 to 26.

[Figure 24]

A schematic cross-sectional view corresponding to a sectional form taken along line X-X in Fig. 18 and illustrating an ejecting operation of the liquid in the liquid-ejecting head with time together with Figs. 19 to 23, 25 and 26.

[Figure 25]

A schematic cross-sectional view corresponding to a sectional form taken along line X-X in Fig. 18 and illustrating an ejecting operation of the liquid in the liquid-ejecting head with time together with Figs. 19 to 24 and 26.

[Figure 26]

A schematic cross-sectional view corresponding to a sectional form taken along line X-X in Fig. 18 and illustrating an ejecting operation of the liquid in the

liquid-ejecting head with time together with Figs. 19 to 25.

[Figure 27]

A schematic perspective view of an ink-jet recording apparatus 600 which is an example of a liquid-ejecting apparatus to which the liquid-ejecting head according to the present invention can be installed and applied.

[Description of Reference Numerals or Symbols]

- 13 ... head
- 14 ... ink groove
- 15 ... heating head
- 16 ... protective film
- 17-1, 17-2 ... electrodes
- 18 ... heating resistor layer
- 19 ... heat accumulating layer
- 20 ... substrate
- 21 ... ink
- 22 ... ejection orifice (minute opening)
- 23 ... meniscus
- 24 ... ink droplets
- 25 ... recording medium
- 26 ... a number of grooves
- 27 ... glass plate
- 28 ... heating head
- 40 ... ink bag
- 42 ... stopper
- 44 ... waste ink absorbing member

45 ... ink cartridge
51 ... sheet feeding part
52 ... sheet feeding rollers
53 ... sheet discharge rollers
61 ... blade
62 ... cap
63 ... ink absorbing member
64 ... ejection-recovery portion
65 ... recording head
66 ... carriage
67 ... guide shaft
68 ... motor
69 ... belt
70 ... recording unit
71 ... head portion
72 ... air passage
600 ... ink-jet recording apparatus
601 ... ink-jet head cartridge
602 ... driving motor
603, 604 ... driving force-transmitting gears
605 ... lead screw
606 ... spiral groove
607 ... carriage
607a ... lever
608 ... guide
609 ... platen roller
610 ... paper pressure plate
611, 612 ... photocouplers

613 ... support member
614 ... cap member
615 ... ink-sucking means
616 ... opening in the cap
617 ... cleaning blade
618 ... moving member
619 ... body support
620 ... lever (for initiating suction)
621 ... cam
832 ... ejection opening
832a ... projected portion
832b ... recessed portion
931 ... electrothermal conversion element (heater,
ink-ejecting energy generating element)
933 ... ink feed opening (opening)
934 ... substrate
935 ... orifice plate (ejection-opening plate)
935a ... ejection-opening face
936 ... ink flow path walls
936a ... partition wall
940 ... ejection opening part
1337 ... bubbling chamber
1338 ... liquid flow path
1141 ... grooves
1141a ... top
100 ... ink-jet recording head
101 ... bubble
102 ... meniscus

1001 ... liquid tank
 1006 ... driving part for movement
 1008 ... casing
 1010 ... recording part
 1010a ... carriage member
 1012 ... cartridge
 1012Y, 1012M, 1012C, 1012B ... ink jet cartridges
 1014 ... guide shaft
 1016 ... belt
 1018 ... motor
 1020 ... driving part
 1022a, 1022b ... roller units
 1024a, 1024b ... roller units
 1026 ... recovery unit
 1026a, 1026b ... pulleys
 1028 ... paper
 1030 ... conveying device
 C ... wet ink
 F_M ... receding direction of the meniscus
 F_C ... opposite direction to the receding direction
 of the meniscus
 G ... center of gravity
 I ... ink
 I_a ... Main droplet (liquid, ink)
 I_b, I_c ... liquid (ink)
 I_d ... ink attached to the groove portion
 I_e ... ink remaining in the liquid flow
 L ... line from the liquid chamber (ink feed opening)

to the ejection opening

N_1 ... width of the bubbling chamber

N_2 ... length of the bubbling chamber

O ... center of the ejection opening

P ... feeding direction of the paper

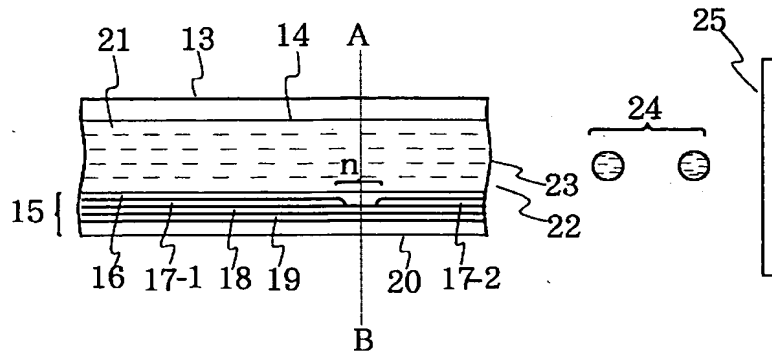
R ... rotational direction of the belt

S ... direction substantially perpendicular to the
feeding direction of the paper

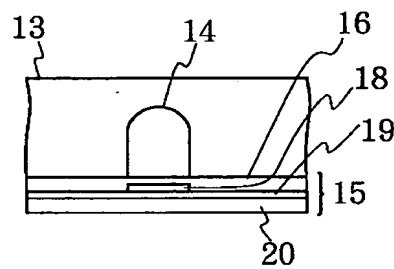
W ... width of the partition wall

【書類名】 図面 [Name of the Document] Drawings

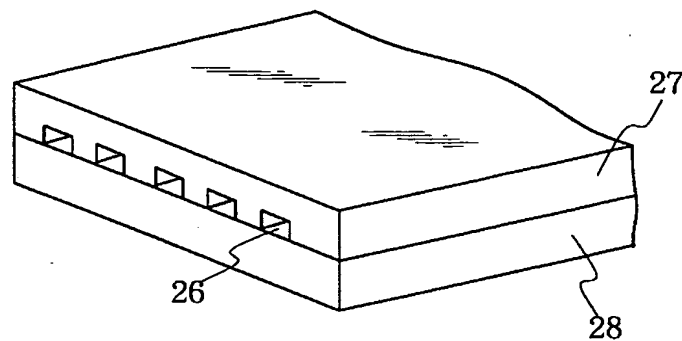
【図1】 Fig. 1



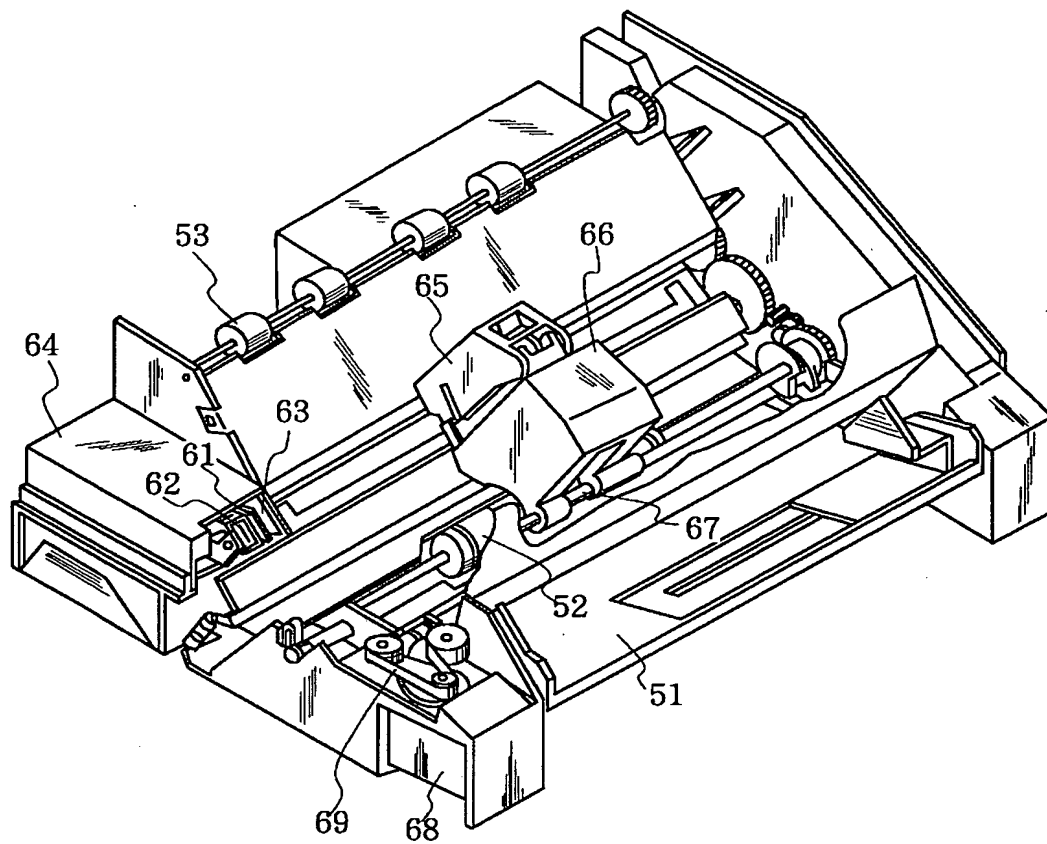
【図2】 Fig. 2



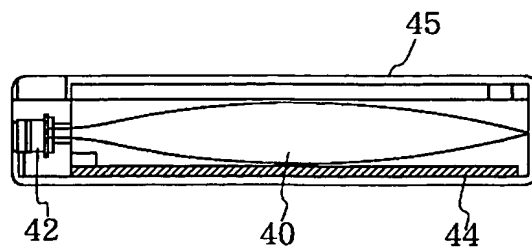
【図3】 Fig. 3



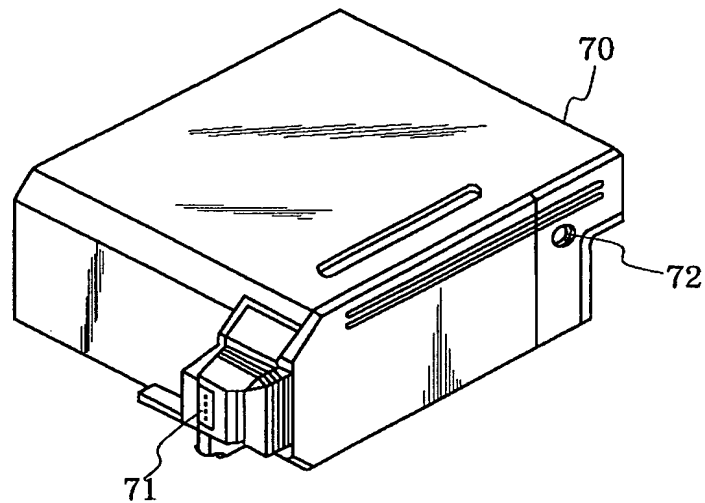
【図4】 Fig. 4



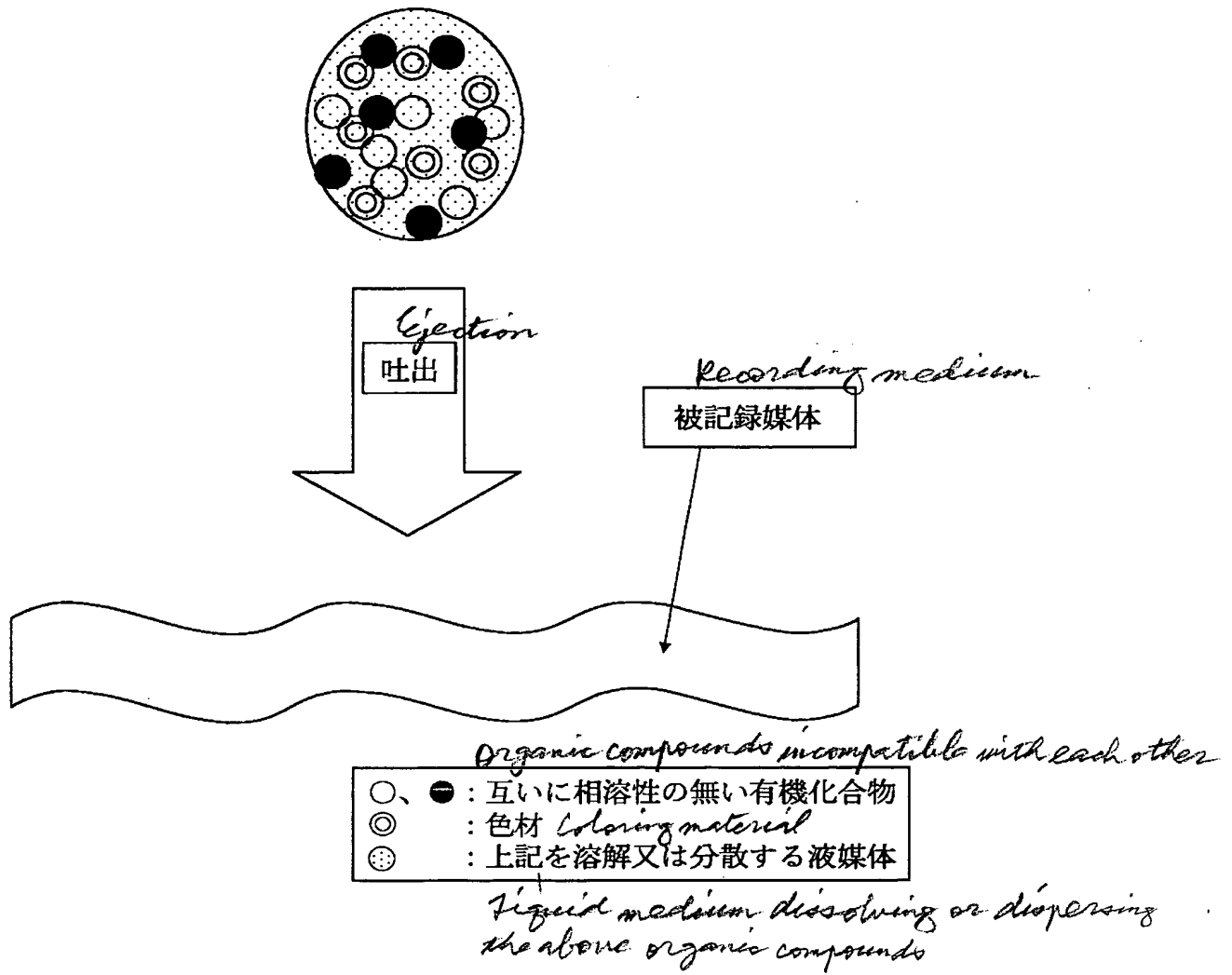
【図5】 Fig. 5



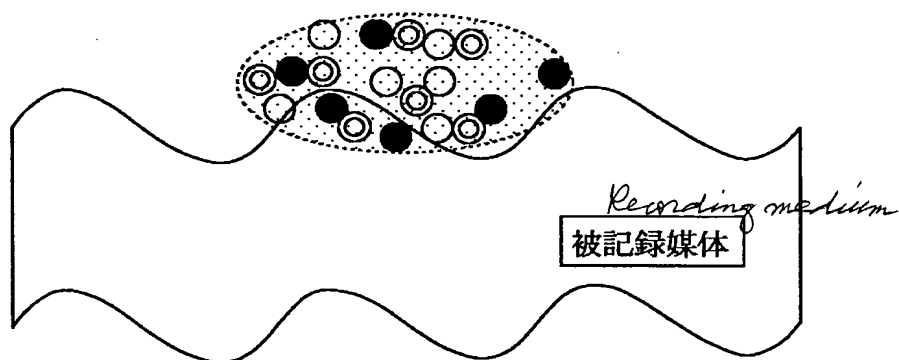
【図6】 Fig. 6.



【図7】 Fig. 7



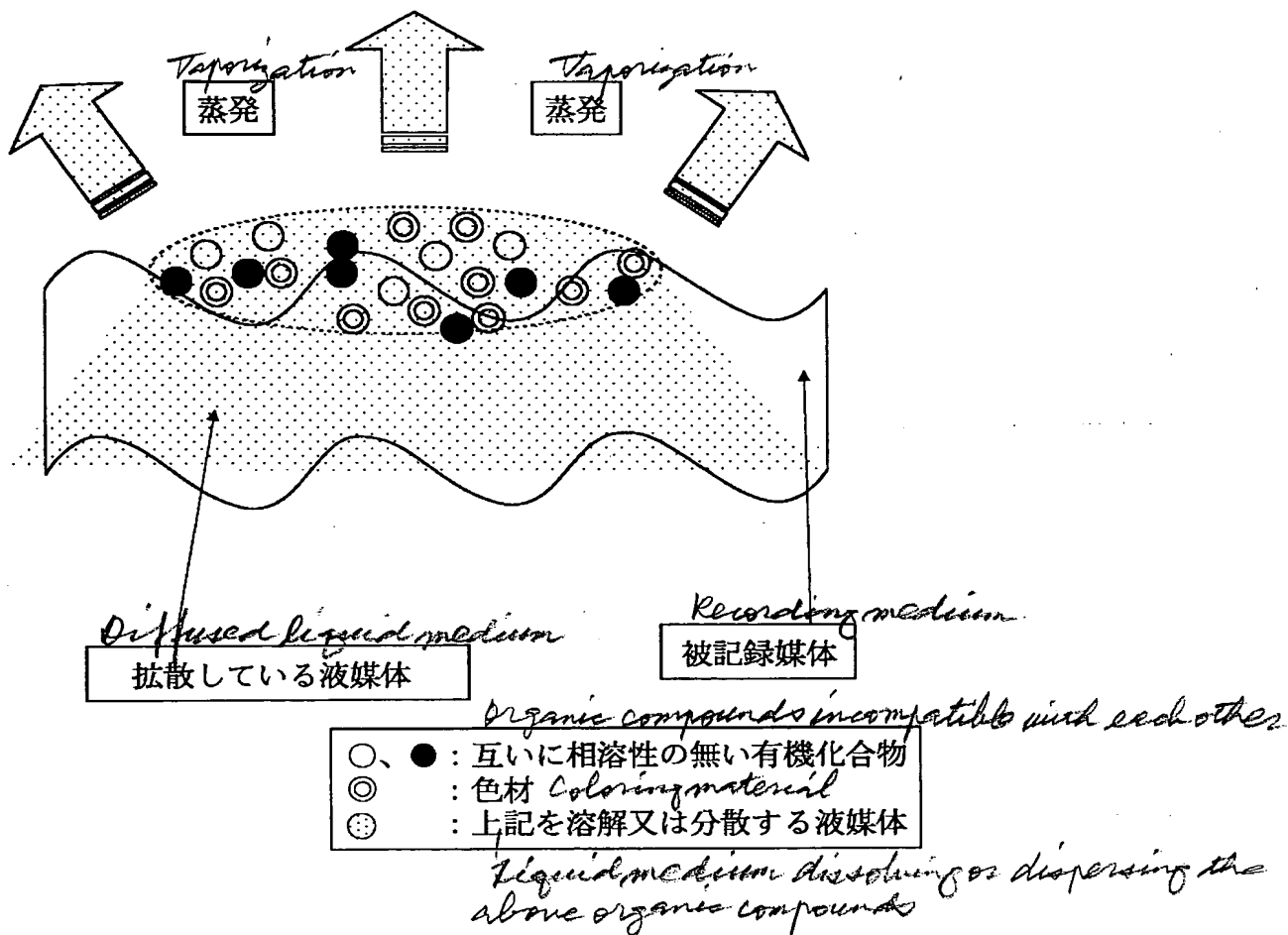
【図8】 Fig.8



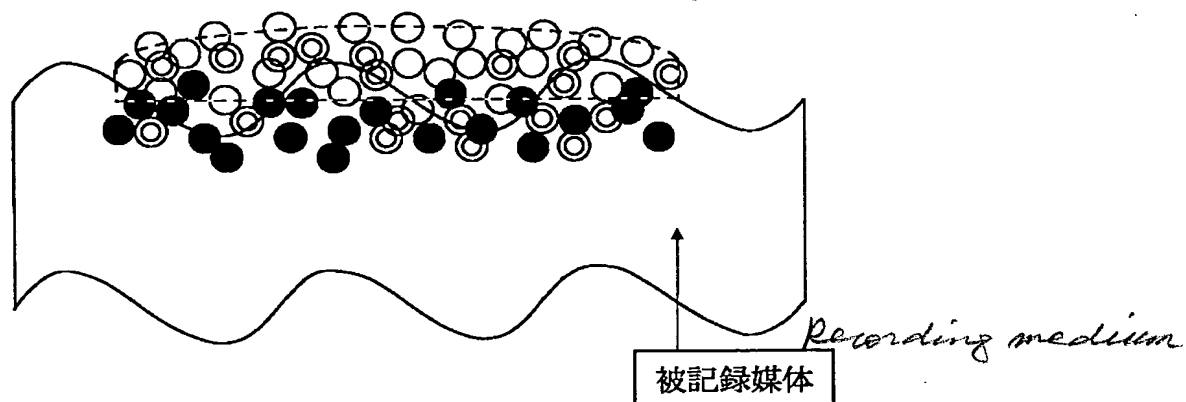
- | | |
|-----|------------------------|
| ○、● | : 互いに相溶性の無い有機化合物 |
| ◎ | : 色材 Coloring material |
| ⊙ | : 上記を溶解又は分散する液媒体 |

Organic compounds incompatible with each other
Liquid medium dissolving or dispersing the above organic compounds

【図 9】 Fig. 9



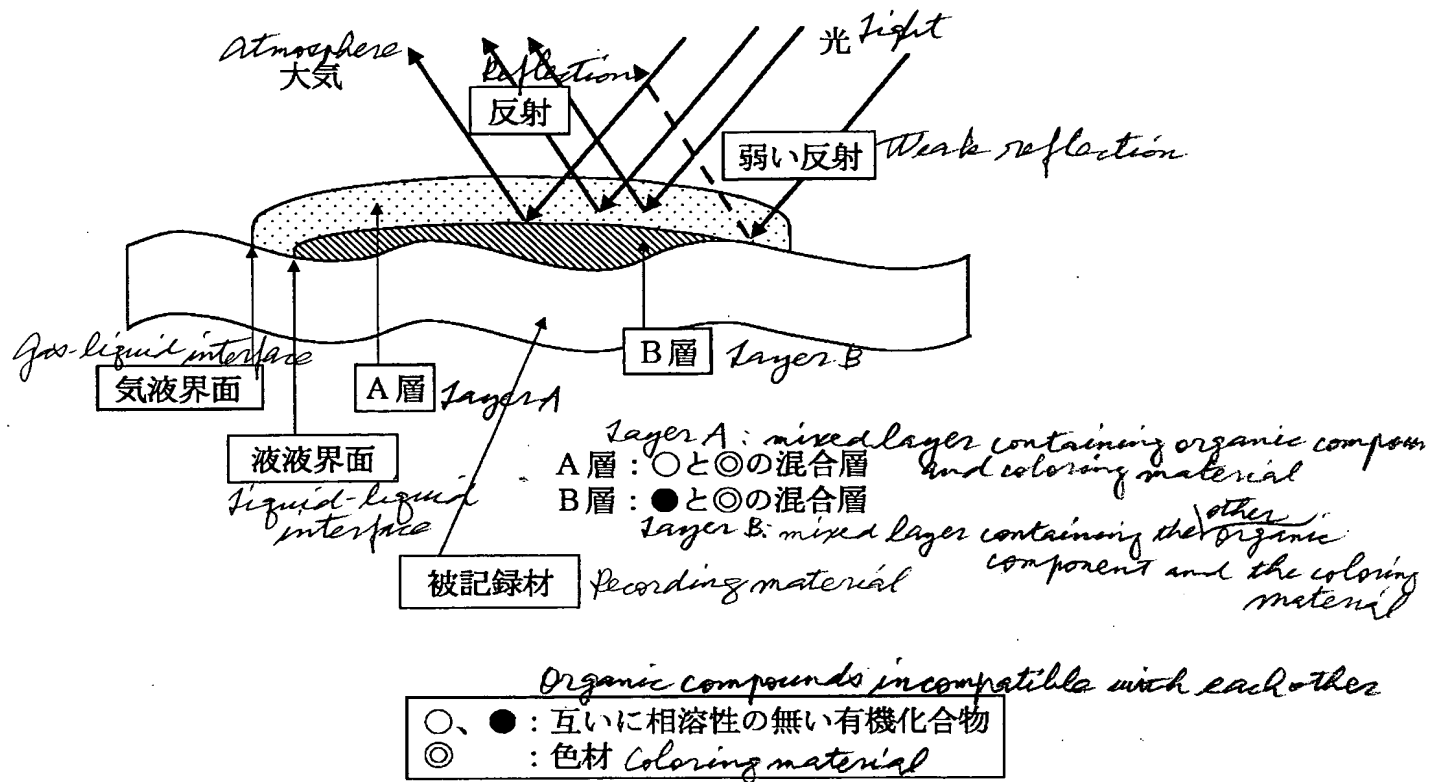
【図10】 Fig.10



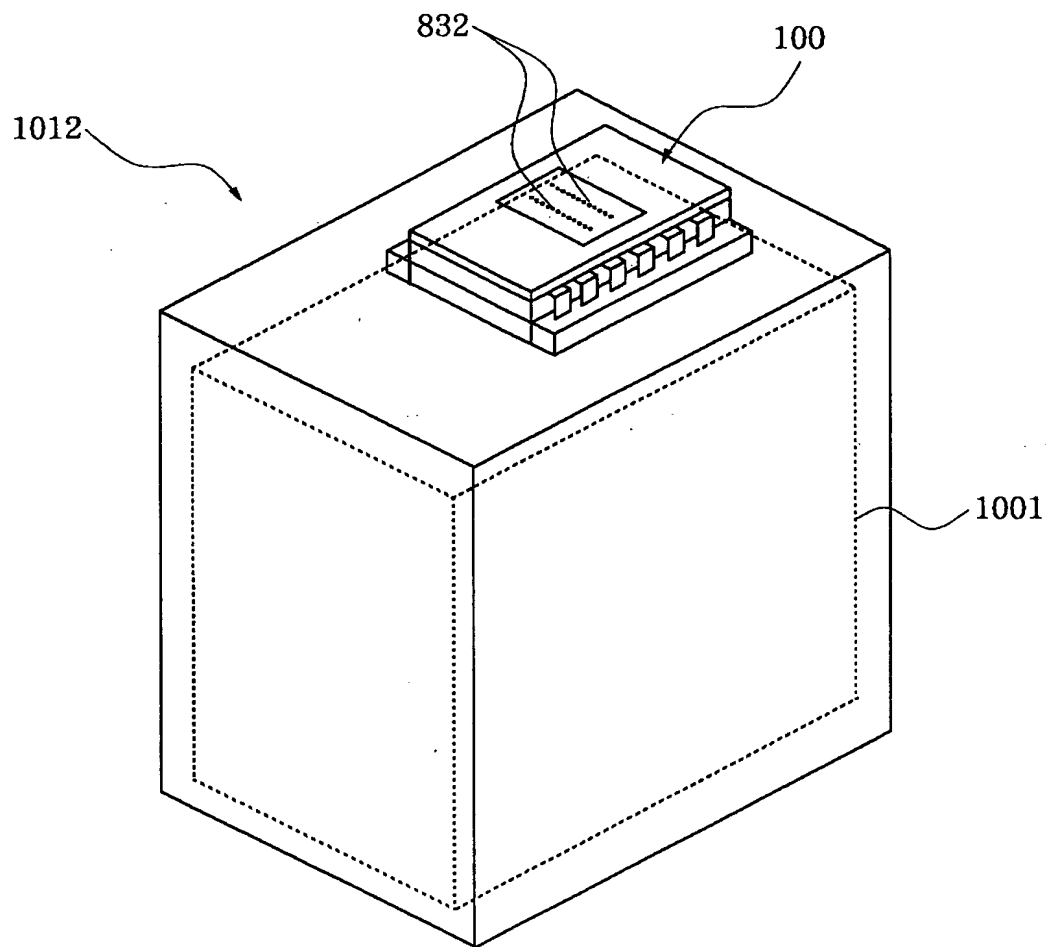
Organic compounds incompatible with each other

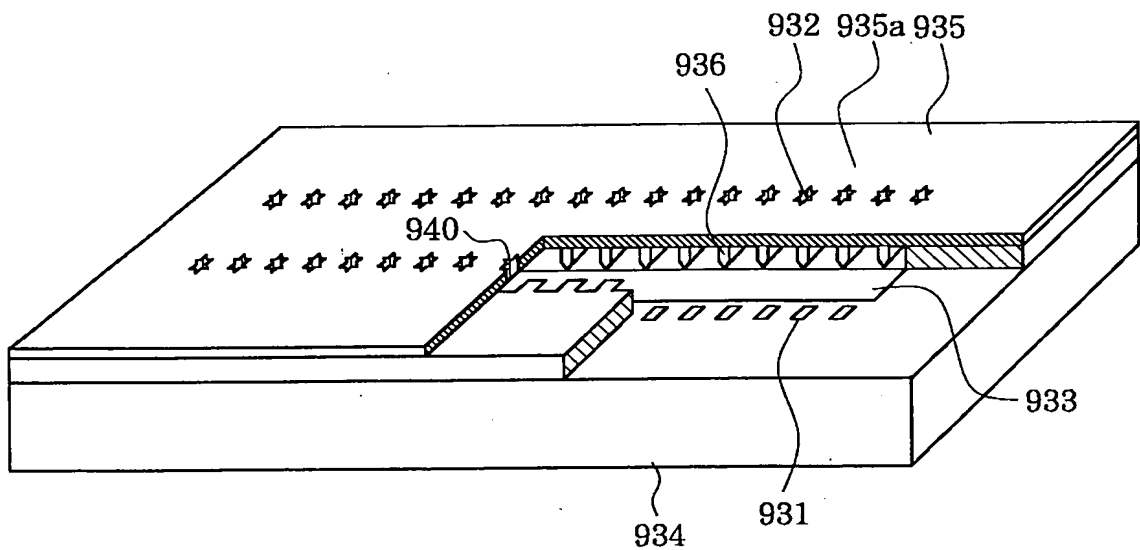
○、●	: 互いに相溶性の無い有機化合物
◎	: 色材 Coloring material

【図11】 Fig. 11

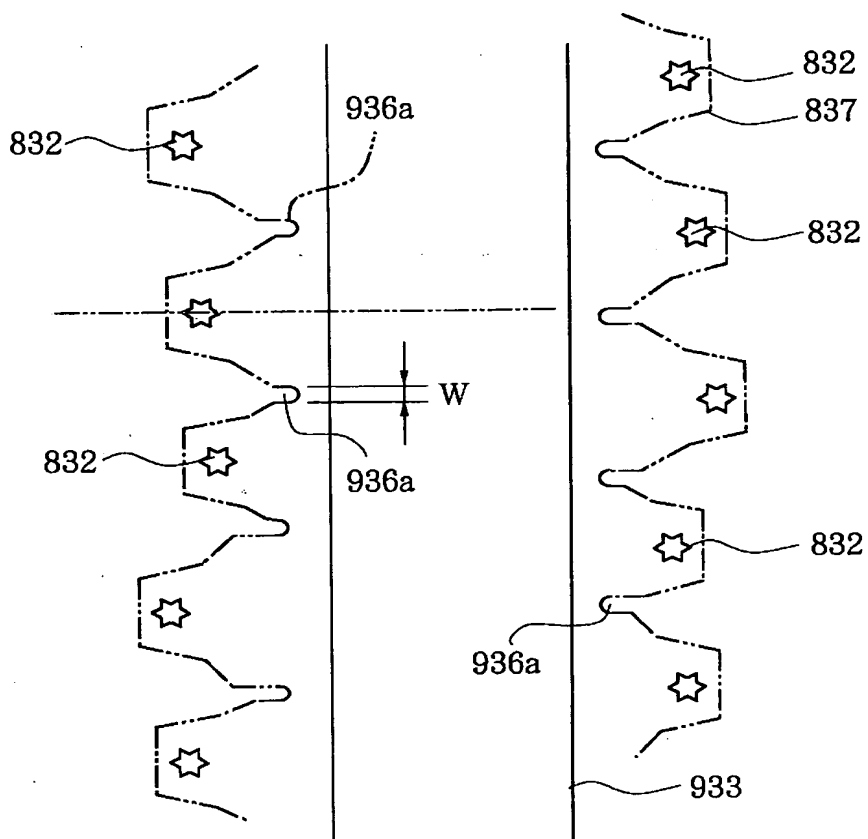


【図13】 Fig. 13

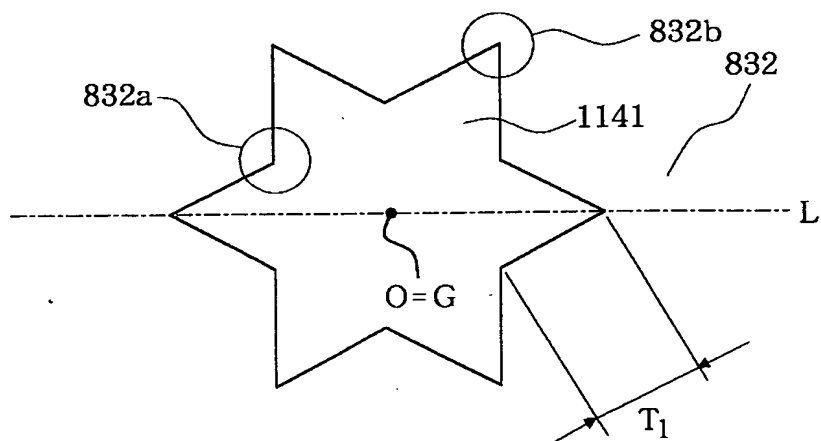




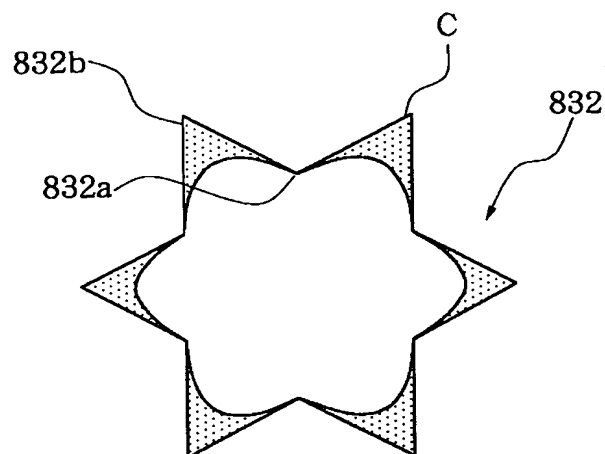
【図15】 Fig. 15



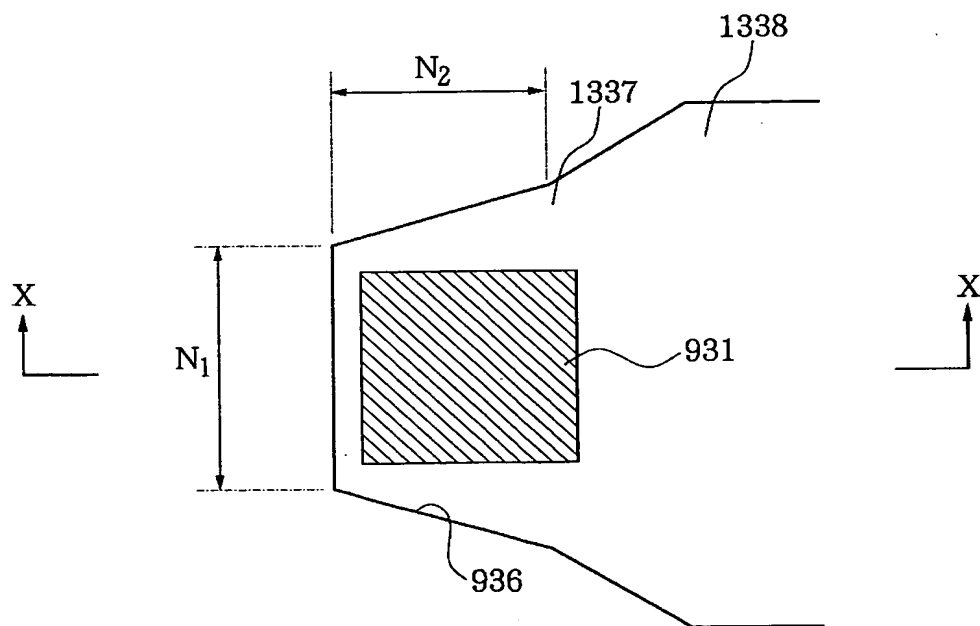
【図16】 Fig. 16



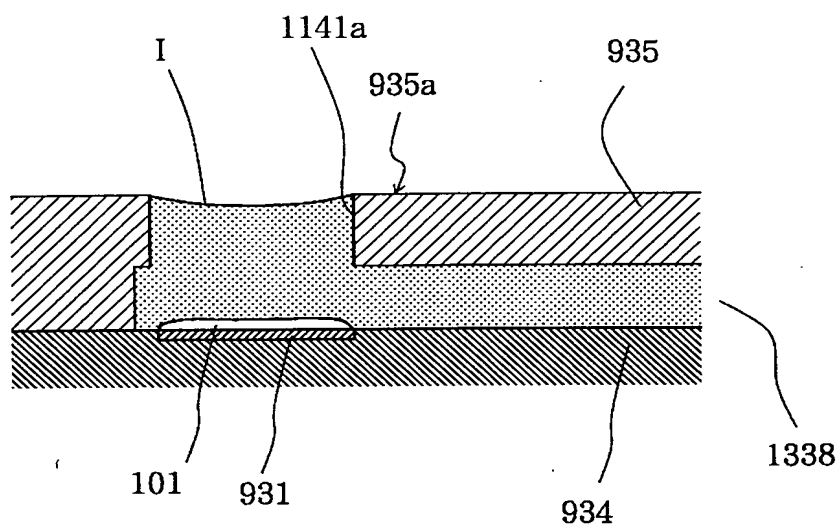
【図17】 Fig. 17



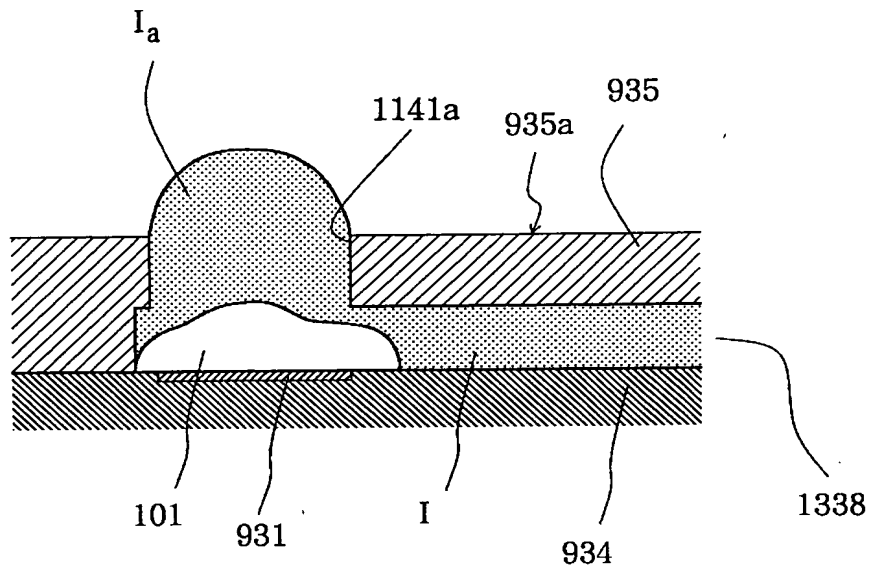
【図18】 Fig. 18



【図19】 Fig.19

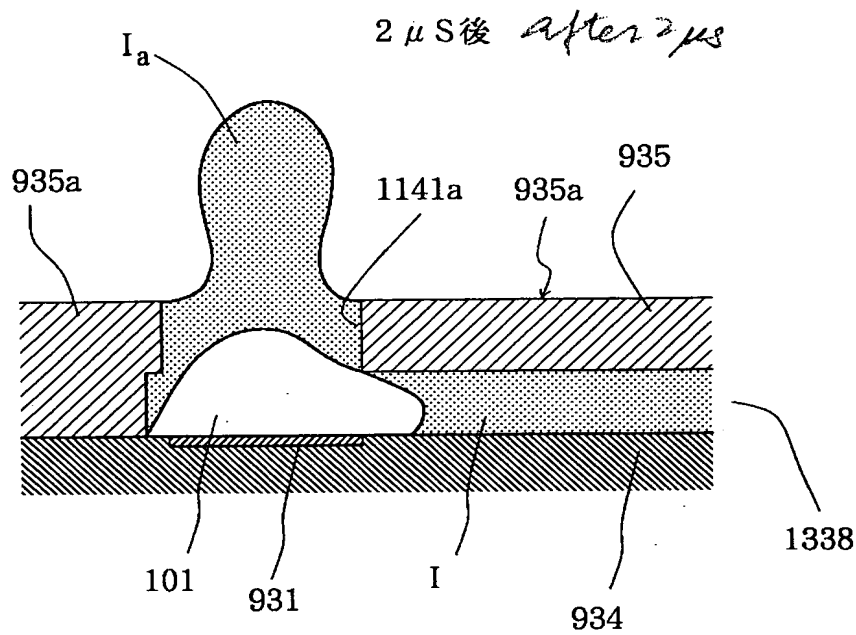


1 μ S後 *after 1 μ s*

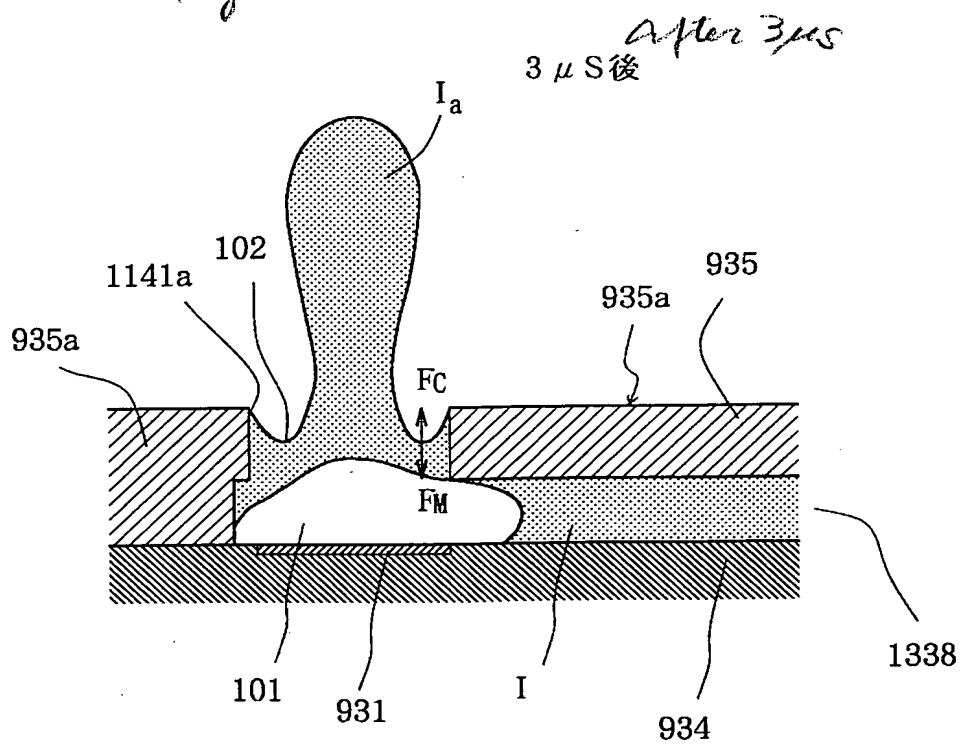


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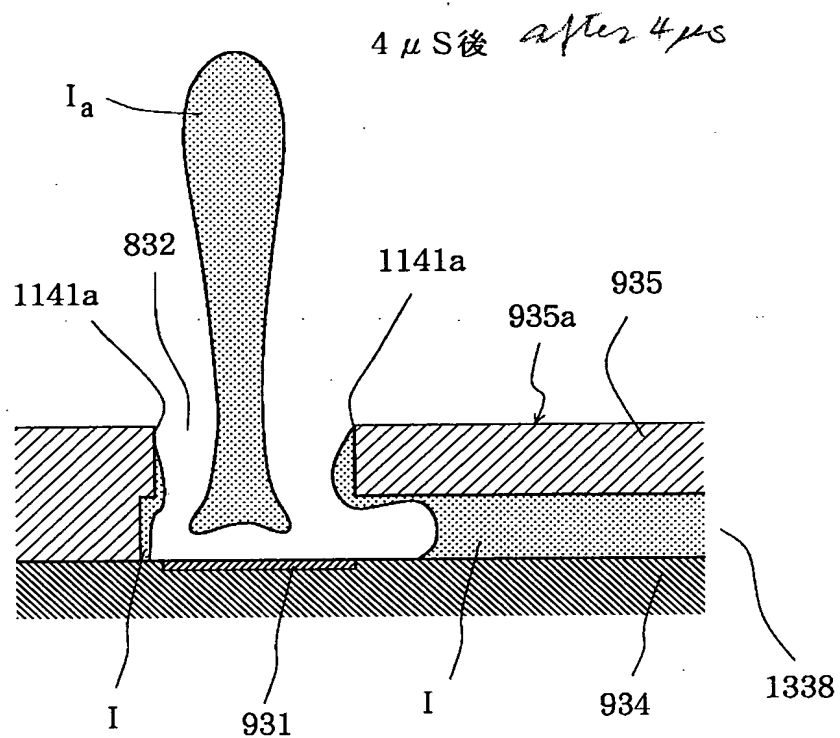
【図21】 Fig. 21



【図22】 Fig. 22

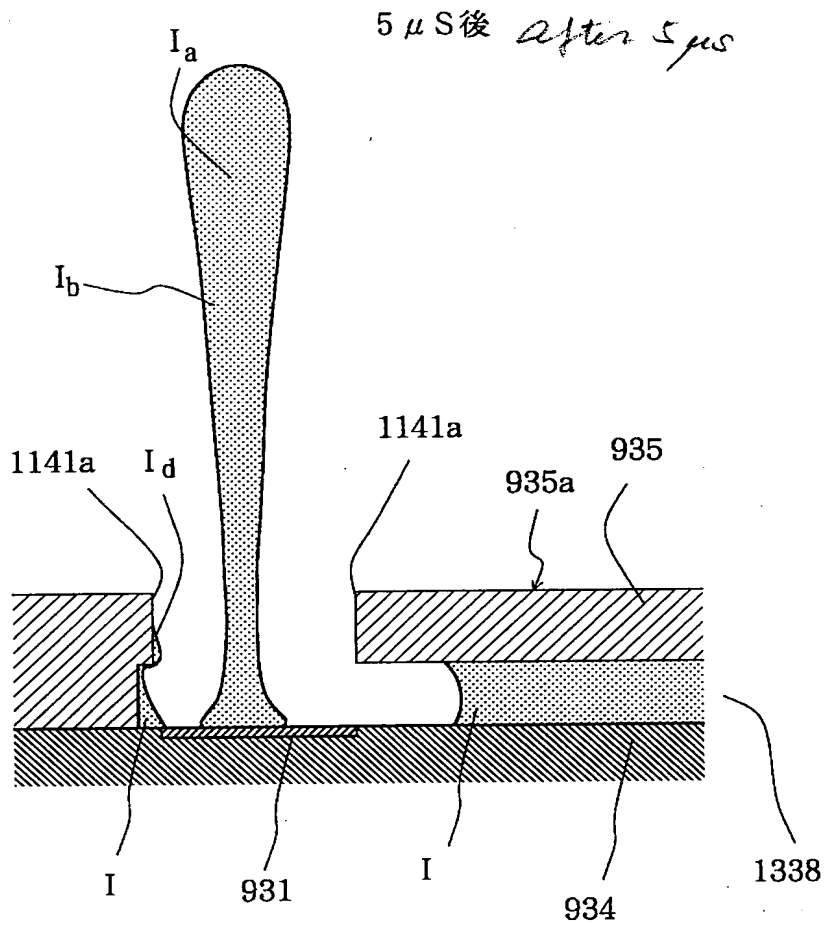


【図23】 Fig. 23

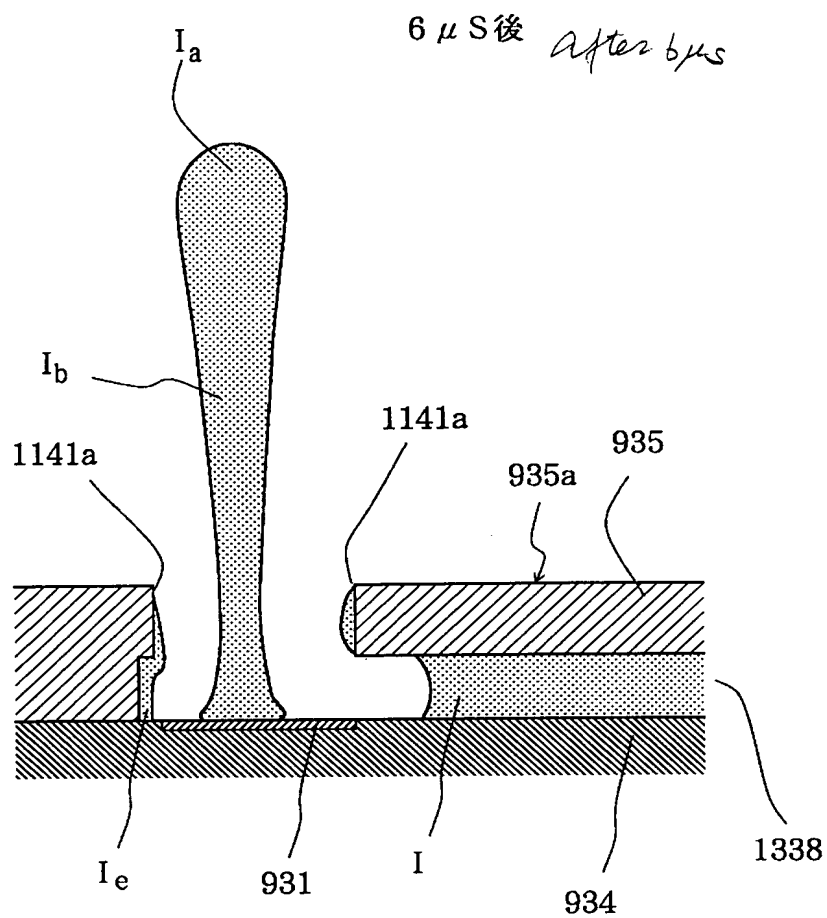


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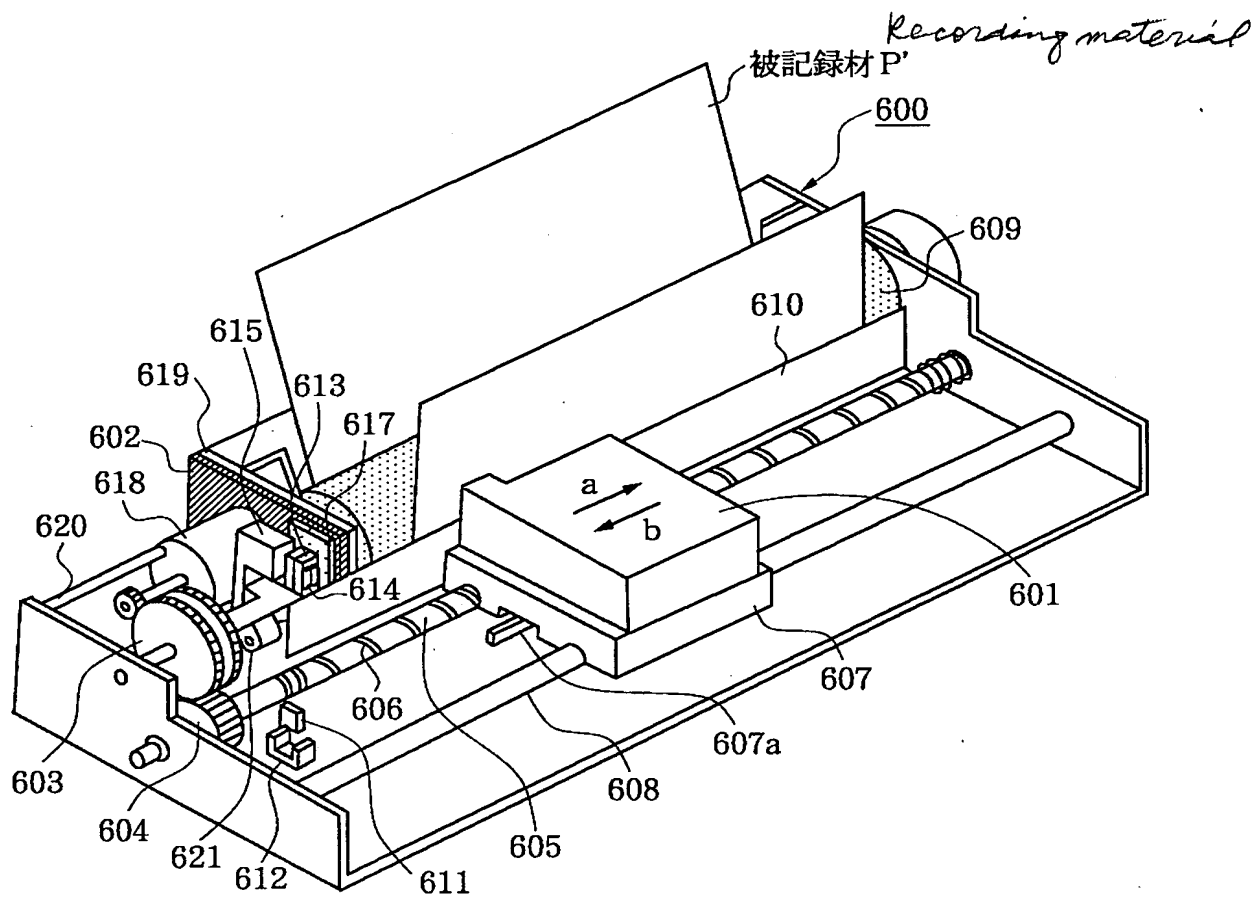
【図24】 Fig. 24



【図 2 5】 Fig. 25



【☒ 27】 Fig. 27



[Name of the Document]

Abstract

[Abstract]

[Object]

An object of the present invention is to provide an ink which can provide a recorded article obtainable by fully making good use of the fluorescence properties of the coloring material, and being excellent in print quality including coloring ability, said ink being capable of enhancing the stability and reliability of the recorded article, and capable of effectively suppressing the deterioration with time of the fluorescence intensity of the recorded article, as well as an ink-jet recording process using such an ink, a recorded article obtained by the recording process, and instruments using such an ink.

[Means for Achieving the Object]

Disclosed are an ink comprising: two combined organic compounds which are incompatible with each other; a coloring material exhibiting fluorescence properties of not more than 1.5 % by weight; glycol having the vapor pressure of not higher than that of diethylene glycol; and a liquid medium for dissolving or dispersing these material therein, as well as an ink-jet recording process employing such ink, a recorded article obtained by such a process, and instruments utilizing such ink.

[Elected Drawing]

None